The Birth of Glow Discharge Chemistry (aka PECVD) ~ and involvement of the Author in a Lifetime pursuit of Semiconductors

by R C G SWANN CEng MIET MIEEE

This paper documents some of the research performed by the author at Standard Telecommunication Laboratories, Harlow, Essex (1959 -1966) and subsequently at the Shockley Laboratories in Palo Alto, California (1966 - 1968) and at ITT Semiconductors in West Palm Beach, Florida (1968 - 1971). The main body of the paper is focussed on the development and continuing success of the glow discharge process particularly over the last 50 years. This paper also extends into the author's role of Corporate Auditing of Semiconductor Suppliers and their technologies, during the second half of a career in semiconductors, implemented at ITT and subsequently at their successor, Alcatel ,also in Telecommunications.

Introduction to Standard Telecommunication Laboratories:

Standard Telecommunication Laboratories (STL), located on a 17acre site, London Road, Harlow, Essex, England was a purpose built facility completed in August 1959 by Standard Telephone and Cables (STC) which, in turn, was owned by the industrial conglomerate International Telephone and Telegraph Corp. (ITT) of New York. Richard (Dick) Swann was amongst the first transferees to STL in September 1959 and awaited completion of the designated lab.

The organisation comprised around 500 staff, extending to 1000 staff at its peak, mainly of scientists and engineers with personnel coming from STC Labs located in Enfield, Middlesex. and from Ilminster, Somerset; the latter under the leadership of Henry Wolfson. Swann came from the latter organisation in 1959, where he was previously engaged in the development of thermistors and then transistors. This early work on transistors will be lost in the mists of time as will be the small laboratory on the site of the old Dowlish Ford Mills rope factory at Ilminster which pioneered and manufactured thermionic valves on this site in the 1940s, followed by development of Thermistors and Transistors (Point Contact and Junction Alloy Transistors) in early 1950s where Swann worked, under Tony Settrington (Thermistors) and Stan Sheppard and Geoff. Walker (Transistors), in the role of laboratory assistant,

STL is acknowledged as the birthplace of a number of significant inventions including optical fibre communications by Charlie Kao and George Hockham and recognised by a Nobel prize awarded to the former. Prior to that work, Pulse Code Modulation had been invented by Alec Reeves whilst working at the ITT Labs in Paris before continuing his work on optical communications at STL. Significant work was also performed on III/V Semiconductor Compounds and associated devices under Chris Dobson and Peter Selway. Novel switching devices using glassy layers sandwiched by two metal electrodes and high voltage junction bevelled transistors as well as the technique of fibre pulling for low loss optical fibres were developed under Cyril Drake and variously assisted by Ken Ellington,Tom Cauge, Ian Scanlon and others. Also, high atmospheric pressure research was carried out using anvils and hydraulic presses to create synthetic diamonds under Prof. Colin H. L. Goodman and Dr. John Lees.
STL, acquired in 1991 by Northern Telecom (headquartered in Canada and later known as Nortel) was integrated into their Bell Northern Labs. In mid 2000 Nortel filed for Chapter 11, signalling the ultimate demise of STL and the end of around 50 years of

significant scientific inventions. A more complete history of STL , may be found on Wikipedia: 'A Brief History of STL' by Vi Maile.

The Birth of Glow Discharge Chemistry for Inorganic Thin Films:

This chapter is focused on the birth of glow discharge chemistry, at STL leading to the deposition of a range of materials hitherto thought impossible to create at such low temperature. This fundamental finding and technique of enabling chemistry at temperatures well below those used in pyrolytic decomposition reactions, is still paving the way into the new nanotechnologies such as carbon nanotubes and graphene material as well its use for fabricating micro-cavity OLEDs (Organic Light Emitting Diodes) and Solid State Lithium Ion Batteries. Studies in the bio-medical field are emerging where surface treatments of materials may be advantageous for implanted devices with research in Japan on substrates for cell growth.. The plasma chemistry concept has already resulted in a multi-billion dollar business for the production of semiconductor integrated circuits (ICs), Thin Film Transistors (TFTs) for flat panel displays, LEDs and solar cells apart from the manufacture and sales of plasma deposition equipment and the provision of a range of material depositions on customers substrates by service labs.

The fundamental principle continues to spawn new studies and is the subject of many research programmes at Institutions and Universities around the World from which many graduates have been awarded their MSc or PhD (see Appendix A) involving more than 40 Universities in more than 30 countries. The selected papers with their respective citations, on the original work, demonstrate that glow discharge chemistry still evokes the imagination and curiosity of the researcher even up to the present year (2015) nearly 50 years later. It also shows that universities and laboratories all over the World have been, or are still involved. including those in:
Algeria, Australia, Belgium, Bulgaria, Brazil, Canada, China, Czech Republic, Colombo, Finland, France, Germany, Holland, India, Iran, Iraq, Italy, Ireland, Japan, Mexico, Poland, Portugal, Romania, South Korea, Spain, Switzerland, Taiwan, Turkey, UK and the USA. The list should include other countries including Lithuania and the former USSR, and also more papers from Taiwan, South Korea and Japan where it is known that extensive work has been performed in this field, however complete manuscripts are not always freely available or translated into the English language, thus making it difficult to read the citations. In some cases there are no citations related to the original work and this typically applies to the new nano technologies which have not been included in this paper.

The derivation of the basic invention was an outcome of early work in a study of the growth of epitaxial silicon layers on single crystal polished slices of silicon. That process was established using a vertical quartz reaction tube inside which was positioned a carbon or molybdenum susceptor to which radio frequency (rf) energy could be inductively coupled, for localised heating purposes, from an external coil and rf generator.The susceptor also formed the horizontal pedestal for holding the silicon wafer. The quartz reaction tube was fed with a precursor and carrier gas.

A research team was set-up by Dr. Joe Evans (Materials Division Manager) who appointed H. (Henley) F. Sterling (sadly passed away in 2012) whose past experience was in growing single crystal ingots from seed crystals of germanium and then silicon by the Czochralski method using a water cooled crucible and r.f heating. Also. the associated development of float zone polysilicon ingot purification in a water cooled silver boat using r.f. energy and its resultant levitation, for sweeping impurities, held in the molten zone, from one end of the ingot to the other.

A plan was established for the newly assembled team to investigate, firstly. the feasibility and then the optimum conditions for silicon epitaxial growth using three different source chemicals preceded by the design and construction of their respective apparatus. Each process to be managed by an assigned process engineer, namely: Silane (SiH_4) under Swann, Silicon Tetrachloride ($SiCl_4$) under Mike Taylor and silicon iodide (SiI_4) under H. Sterling. The latter process was terminated within 1 year, since process control was difficult. The remaining two processes were further developed and optimised in respect of crystal perfection and growth rates. The author is indebted to D (Dave) J. D. Thomas for sharing his expertise and giving guidance on matters of crystallography as well as the early use of the Scanning Electron Microscope (SEM). The silicon tetrachloride process yielded higher growth rates but the process suffered from auto doping of impurities, transported by the chlorine, from the substrate into the grown layer; not seen in the silane based process due to the absence of the chloride transport mechanism.
It was decided to continue investigations with both processes to ready them for production and to concentrate on enhancing the growth rate of silicon from silane. The approach was to increase the streaming velocity and explore the impact of low pressures by partial vacuum within the reaction tube.

This action by Swann showed, unexpectedly, that no deposition occurred at the susceptor hot zone however after several runs a deposit was observed, unexpectedly, higher up on the cold wall of the quartz reaction tube which was at first thought to be the result of a leak in the system causing a spontaneous reaction between the air and silane (this of course could lead to an explosion). Exhaustive tests showed that no leaks were present and it was then decided to view the reaction chamber in low ambient light conditions, at nightfall, upon which it was evident that a glow discharge or plasma was occurring, resulting in the deposition of amorphous silicon which was more fully explored and published three years later by Chittick, Alexander and Sterling. The significant finding of the feasibility of glow discharge chemistry diverted attention away from silicon epitaxy which was being installed at the production sites of ITT in STC Footscray and Intermetall, Freiburg, Germany; to study this new found chemistry, which we called 'Glow Discharge Chemistry' later referred to as plasma enhanced chemical vapour deposition (PECVD); a misnomer since the plasma is the prime mover of the chemical process and not simply an enhancer. Some others called it PACVD (Plasma Activated Chemical Vapour Deposition, which was more appropriate but we all lost out to PECVD. We demonstrated that thin films can be deposited at room temperature without thermal activation, however the film density and other properties may be compromised.

At STL, we studied the feasibility of performing the chemistry of depositing glassy vitreous/ amorphous silicon films from silane (SiH_4), silicon carbide from silane and methane (CH_4) or methyl silane (CH_6Si), germanium from germane (GeH_4), carbon from methane (CH_4) but concentrated on silicon dioxide from silane and nitrous oxide (N_2O) and especially silicon nitride (Si_3N_4) from silane and ammonia (NH_3) for its potential to support not only ITT's own semiconductor industry but subsequently the Worldwide industry. The latter application was a 'first' in terms of demonstrating capability and obtaining more reliable semiconductor devices when depositing passivation layers of silicon nitride, silicon oxynitride or silicon dioxide, singly or in combination, at a temperature well below that of a thermally activated chemical process for silicon nitride. Publication of these findings was withheld for some considerable time until patent descriptions were written and an Application submitted to the Patent Office in 1964.

Presenting the Glow Discharge Process to The World:

Initially, as shown in Appendix B, French, British and US Patents were applied-for (1964 and 1965) in respect of the basic invention in the names of Henley Frank Sterling and Richard Charles George Swann. Following the Patent Applications, Swann was directed by STL Management to present the glow discharge findings at various conferences and to publish in scientific journals as detailed in Appendix C and D. It was, however, at The Physics Society Exhibition in Manchester (April 1965) where the glow-discharge equipment, designed and built at STL, was demonstrated by Swann and Dave Thomas, which resulted in a Worldwide interest. Many enquiries and requests for feasibility and sample preparations were made including: part of a jet engine turbine blade, nylon material from the fabric/garment industry, paper from the newsprint industry, leather from the shoe industry, strip steel from a steel mill, and anti reflective coatings on optical glass etc.
Papers were soon presented by other scientists from notably the USA including IBM (The Worldwide leader in Computers), Texas Instruments (representing the Semiconductor Device field) and Applied Materials (representing the Semiconductor Equipment Field).

Transfer to the Shockley Labs, Palo Alto, California:

In early 1966, Swann was invited by the Vice President and Deputy General, Technical Director, ITT New York (Steward (Stu) Flaschen) and Dr Joe Evans to transfer to the ITT Shockley Laboratories, Page Mill Road, Palo Alto, California, to continue the glow discharge studies and contribute to the emergence of the integrated circuit technology (in the yet to be named “Silicon Valley”). The Shockley Labs were originally established in Mountain View, California by William Shockley, co-inventor of the transistor, and the new purpose built Lab on Page Mill Road was subsequently owned by the Clevite Corp. and then acquired by ITT in 1965.

The first step by Swann, at the Shockley Labs, was to build the plasma equipment and study the properties of the resultant insulating layers in the context of the emerging metal gate PMOS/CMOS device technology. State of the art measuring equipment for thin films was made initially available by the nearby Stanford Medical School whilst useful contacts were made at Stanford University with assistance provided to study the plasma by using a Langmuir Probe, The most significant findings were in respect of demonstrating the excellent barrier to sodium when employing silicon nitride as opposed to the standard silicon dioxide dielectric; as well as the excellent compatibility of the plasma deposition process with existing semiconductor technologies. The electrical charge impact on the MOS gate was also studied in detail. Further experimental work was carried out to demonstrate the feasibility of doping silicon using elemental species by using plasma deposited layers for which a patent was filed by Swann and Cauge in March 1968.

Transfer to ITT Semiconductors, West Palm Beach, Florida:

In 1968, Swann was asked by ITT HQ in New York to set up a new state-of-the-art cleanroom within their existing bipolar transistor/integrated circuit operation in West Palm Beach, Florida. The plasma process was scaled-up in a 10 inch bell jar to handle multiple wafers and in addition early pioneering work was performed on a poly crystalline silicon gate technology which of course became the industry standard. Patents were filed in January 1971 by Swann and Penton and in September 1973 by Harlow, Swann, Penton and Bakker in the context of silicon gate NMOS technology. A study of the properties of

Silicon Dioxide, in a glow discharge, from the precursor gases of SiH_4 and CO_2 were published by Swann and A E Pyne , in 1969. A Silicon gate MOS Integrated circuit was also demonstrated by converting a licensed Fairchild Multiplexer from Metal (Aluminium) Gate to Silicon Gate MOS with much improved performance and subsequently its conversion from PMOS to NMOS technology.

At the conclusion of Swann's career in semiconductor research, a total of 13 patents were issued in co-authorship with different collaborators at various ITT laboratories. The subject areas were in the realm of either thin film glow discharge chemistry or in novel semiconductor device structures (See Appendix B). The Patents issued, embraced 5 countries, namely: the UK, USA, Canada, Germany and France.

A list of Publications, Presentations and Exhibits up to this point and beyond are listed chronologically in Appendix C.

<u>Return to STL Harlow:</u>

In 1971, Swann was reassigned to STL Harlow as Chief Scientist, reporting to ITTs Worldwide Semiconductor Corporate Technical Director (Dr Herb, Renner) in New York. The objectives were to oversee the setting-up of a silicon gate process to yield a 4x4 Crosspoint electronic switch for ITTs state-of-the-art switching system, as well as overseeing research programmes in ITT's research and manufacturing locations in Footscray - England, Freiburg - Germany, West Palm Beach - Florida and at Shelton - Connecticut.

<u>A Career Change in Semiconductors:</u>

In 1974, ITT Europe HQ in Belgium, requested assistance to establish a system for the assessment and control of their semiconductor component suppliers of which there were many new emerging suppliers and new technologies. The Supplier Assessment Program embraced the setting up of Standards and a System for on-site assessment visits to Semiconductor Suppliers to evaluate their capability from an Organisational, Quality and Manufacturing point of view but even more importantly to record a confidential detailed, step by step, process flow chart with baseline parameters to assess integrity, reliability, manufacturability and the ability to monitor change especially in the context of the fast growing 'custom integrated circuit field'. Reporting was made to Corporate Purchasing with Supplier Reports going to all Component Managers in all the Worldwide Telecom operations of ITT. Swann joined an existing group of Component Managers at The ITT Europe Engineering Centre in Harlow, in the role of Manager of Semiconductors-Integrated Circuits.

The system, established by Swann, was well acknowledged within the Worldwide Corporate Purchasing Department and by all manufacturing operations of ITT as being a sound, cost saving measure (minimising product failures, supply issues and a harmonised procurement system across ITT) and in turn by Suppliers who saw the benefits of the most rigorous third party Audits they had experienced with detailed and constructive critiques. The system was adopted by Alcatel, France upon their purchase of ITT's Telecom. Operations in 1986. This work provided Swann, who was based at the Alcatel HQ in Paris and then at Alcatel ITS in Zug. Switzerland, with a unique incite into the

Worldwide Semiconductor Industry and its technology which in his career spanning 45 years witnessed the evolution from 1 inch to 12 inch diameter silicon wafers (now going to 18 inches) and feature sizes reduced from 10 microns to <0.25 microns with Photolithography moving from In-Contact Printing to Steppers and Laser I-line Projection equipment, wet etching transitioning to dry plasma etching, MOS gates moving from aluminium to poly silicon, the universal application of PECVD and planarisation progressing from isoplanar structures and reflow glasses to CMP (Chemical Mechanical Polishing).

The statistics, of the supplier and technology assessment activity over 25 years, upon reflection, are quite amazing e.g.

*. Assessment of > 60 Semiconductor Companies
*. Visited and assessed > 115 Wafer Fabrication manufacturing locations
*. Assessed a Total number of Wafer Fab. Lines > 250
*. Similar statistics were accrued for Assembly and Test Operations Worldwide.
*. Travelled on 3000 flights and 130 Airlines and visited 47 different Countries

A few of the extreme Audit findings identified, and not previously declared, included;

★ In one case the lack of a Quality Department, in another, the lack of a Quality Manager, another case where the Quality function was directly involved in production and in many cases the lack of meaningful documentation and statistical process control.

★ A Wafer Fab line had been shutdown for more than 2 weeks whilst a source of contamination had still not been identified during the Audit.

★ A factory in China, where excellent documentation prevailed, was 'set-up' by the Company, for the ITT assessment inspection, with workers performing tasks but, in fact, it was found that the factory had not been in production for more than one year! Plastic moulding compound was stored in a cafeteria refrigerator together with food!

★ Due to manufacturing difficulties a contracted Company had subcontracted part of the process and in another case the entire process, both in violation of the Contract terms.

★ The layout of a factory floor was better known by the Inspection team than by the Manager hosting the Audi .

★ Some bizarre events, disturbing the ongoing/planned inspection, included: a leaking poisonous gas, a fire in the wafer fab, the death of a worker falling through the roof of the factory and a severe destructive earthquake.

★ The Semiconductor Corporate HQ of a large European Company did not know of the existence of its wafer fab and assembly line in the South Pacific , belonging to another Product Division of the Company.

In summary, a unique career in the silicon semiconductor industry from its inception to its growth in Silicon Valley and beyond. The opportunity to be involved in the grass roots development and patenting of glow discharge chemistry and especially to demonstrate the advantages of silicon nitride in respect of the improved reliability of integrated circuits. To be also at the forefront of development of the silicon gate MOS technology which is still the workhorse of today's technology. Also, perhaps the greatest reward, in that plasma chemistry is still, today, the subject of continuing interest in the development of new technologies and devices, particularly in more than 30 Universities Worldwide, as identified in the attached Document on Citations.

Swann was awarded the coveted 'ITT Ring of Quality' award in June1983 at a ceremony in Lisbon, Portugal for his contribution to Semiconductor Technology and the Quality Control of purchased semiconductor products.

<u>Citations by other Scientists and Engineers:</u>

Finally, this paper is concluded by ten quoted citations which have been extracted from the current list of around 160 citations , to be found in Appendix A:-

- 1966 S.M. Hu IBM System Development Div. East Fishkill, New York, USA
  "It appears that the first published successful attempt to prepare films of silicon nitride is the recent work of Sterling and Swann".

- 1976 S. Rosler, Dr W. Benzing and J. Baldo- Applied Materials, Santa Clara,California
  (The start of what became the largest supplier of production Plasma Deposition Equip.)
  "In 1967, Swann et al reported that, 'Plasma promoted low temperature Nitride is suitable for passivating silicon planar devices', the very topic that is creating all the interest today".

- 1988 Prof. W.E. Spear, Dundee University, 'The Bakerian Lecture' 1988 Proceedings of The Royal Society, London.

"Amorphous silicon (a-Si) deposited in a glow discharge plasma, an approach pioneered at the STL laboratories in Harlow, (Sterling and Swann 1965) proved to be an ideal model and by the mid-1970s we had established the unique electronic properties of a-Si and also recognized the applied potential of this dopable and electronically controllable thin film material".

- 2003 D.M. Mattox - President of The Society of Vacuum Coaters, Albuerquerque,N.M.
  Historical Timeline of Vacuum Coating and Vacuum/Plasma Technology:
  - -1678 Picard's glow (Plasma)
  - -1720 Electrical (glow) discharge generated (Hawksbee)
  - -1885 Inductively excited plasma (HIttorf)
  - -1921 Plasma desorption from surfaces (Campbell)
  - -1965 Plasma enhanced CVD (Sterling and Swann).

- 2004 Kushner M.A. - University of Illinois, Urbana, USA
  "Continuity in Plasma Processing"
  - -1790's First Glow Discharges (Hawksbee)
  - -1830's Glow Dischardes (M. Faraday)
  - -1890's RF Discharges (N. Tesla)
  - -1960's PECVD (Sterling and Swann)

- 2006 J. Poortman and V. Arkhipov - IMEC Leuven, Belgium
  "The first amorphous silicon layers were deposited in a radio frequency driven glow discharge using silane.(Ref. Sterling and Swann).
  The radio frequency glow discharge method, today known as PECVD, is still the method most commonly used, both in the laboratory and on an industrial scale".

- 2009 F. Zhu and A. Madan - MV Systems, Golden, Colorado and Gaillard and Miller, University of Hawaii, Honolulu
  " Amorphous silicon (a-Si) is the basis of a multi-billion dollar industry in applications as diverse as active matrix liquid crystal displays (AMLCD), Electro-photography, Image sensors, solar cells etc. The origins of this remarkable commercial success can be traced to the work at STL, Harlow UK 1965 (Ref. Sterling and Swann)".

- 2011 Dr A.F. Flannery - Stanford University, Palo Alto California
  "The earliest reference to the deposition of silicon carbide by radio frequency plasma was by Sterling and Swann. At this time, PECVD was referred to as the glow discharge method of deposition".

- 2012 Dr C Coyle - Dublin City University
  "The 1960s saw the first studies of surface modification using plasma assisted processes (Ref. Sterling and Swann) which focussed on protective coatings and surface activation.
  It is expected that the use of plasma will continue to expand because they have unique capability, are economically attractive and are friendly towards the environment".

- 2014 Dr J.Trask - University of Minnesota, Michigan
  " The earliest example of thin film technology and possibly the most heavily studied, has been hydrogenated amorphous silicon (a-Si). Having been successfully deposited using a plasma discharge for the first time over 45 years ago [17} Ref. H.F.Sterling and Swann.

	PECVD Technical Papers 1966 to 2015 with citations identified by R C G SWANN	*citing:* H. F. Sterling and R C G Swann	**STL Harlow Essex England**	**"Chemical Vapour Deposition Promoted by R.F. Discharge" Solid State Electronics 1965 Vol. 8 Pages 653-654 Google citations = 249 as of 24th Jan 2015**
		R C G Swann, R R Mehta and T P Cauge	**Shockley Labs., Palo Alto California USA**	**"The Preparation and Properties of Thin Film Silicon-Nitrogen Compounds Produced by a Radio Frequency Glow Discharge Reaction" J. Electrochem. Soc. 114, 713 (1967) Google citations = 92 as of 24th Jan 2015**
DATE	AUTHOR(S) & AFFILIATION	TITLE of ARTICLE	Jnl./ Prof. Attainment	CREDIT / CITATION
2014 SEPT	Hanni S École Polytechnique Fédérale de Lausanne Switzerland	Polycrystalline Silicon for High Efficiency Thin Film Photovoltaic Devices	DSc Thesis Presented 19th Sept. 2014	Page 4 1.2 Thin Film Silicon Photvoltaics. Since the manufacture of the first hydrogenated silicon (a-Si:H) layers {Sterling and Swann, Ref.65 {1965} and Chittick Ref. 69 {1969}and the demonstration of their possible doping Spear Ref.75 {1975} and Spear 76 {1976} leading to a first working device Carlson {1976}, thin film silicon has gained a tremendous interest for PV applications.
2014 AUG	Demaurex B Bartlome R Seif J P Et al École Polytechnique, Fédérale de Lausanne Switzerland	Low Temperature Plasma-deposited silicon epitaxial films: Growth and Properties	AIP J. Appl. Physics 116, 053519 (2014)	However, at high temperatures, unintentional dopant and impurity diffusion may also occur, detrimentally affecting the bulk electronic properties of the substrate (eg the charge carrier lifetime) or impairing the properties gained by earlier processing steps. The problem may be circumvented by using plasma enhanced chemical vapour deposition (PECVD) which disassociates process gases at significantly lower temperatures compared to thermal CVD. Ref. Sterling and Swann

2014 JULY	Kirner S Technical University, Berlin, Germany	Development of Wide Band Gap Materials for Thin Film Solar Cells	PhD Thesis (Presented 11/07/2013)	A great technological advantage of amorphous- over crystalline- silicon is the fact that it can be deposited directly as a thin layer onto a foreign substrate by e.g. plasma enhanced chemical vapor deposition (PECVD). This was first shown by Sterling and Swann in 1965.
2014 JULY	Franco A École Polytechnique Fédérale De Lausanne, Switzerland	Monolithic Particle Detectors based on Hydrogenated Amorphous Silicon	PhD Thesis Presented 26th Aug. 2014	3-2 a-Si:H deposition by PECVD In the 50s', amorphous silicon was deposited for the first time by evaporation. The absence of hydrogen resulted in a highly defective material, not suitable for any electronic application like photovoltaic devices or transistors. Eventually, a-Si:H layers started to be deposited by glow discharge .(Ref. Sterling and Swann) of Silane (SiH4), the gas precursor used still today to produce the state-of-the art a-Si:H devices.
2014 JAN	Biriktirme K B Sakararya Universitesi Turkey	Not identified	Thesis Approved 12.01.2014	Google Translation (SIC) The first plasma chemical vapour deposition process comprising the "Glow discharge deposition" was called. Then supported by the plasma CVD (PECVD) began to be referred to as. In 1965, Sterling and Swann discussed about the importance of plasma decomposition of CVD.
2013 DEC	Trask J University of Minnesota USA	Enhanced Crystallization of Amorphous Silico Thin Films by Nano-crystallite Seeding	PhD Thesis	The earliest example of thin film technology, and possibly the most heavily studied, has been hydrogenated amorphous silicon (a- Si:H). Having been successfully deposited using a plasma discharge for the first time over 45 years ago [17] ref. H F Sterling and R C G Swann. Although several alternative deposition methods have emerged in the last few decades, including hot wire deposition and electron beam deposition, a- Si:H is still overwhelmingly grown from plasma dissociation of a silicon containing gas, silane, in a method known as plasma enhanced vapor deposition (PECVD)
2013 NOV	Schouten M Dept. of Electrical Sustainable Energy Delft University of Technology, Holland	The nanostructure of hydrogenated amorphous silicon, examined by means of thermal annealing and light soaking.	MSc Thesis	Hydrogenated amorphous silicon was first produced in the second half of the 1960s by Sterling and Swann, in the context of research into amorphous semiconductors. Whereas previously sputtering and thermal evaporation were used for creating amorphous silicon, Sterling and Swann used a radio frequency discharge glow discharge method with silane as feedstock.

2013 OCT	Morosanu C E Electronic Components Research and Development Centre, Bucharest 30 Romania	Thin Films by Chemical Vapour Deposition	Elsevier ISBN 978-0-44 4-98801-0	1.2 Short History of CVD Thin Films Early PECVD work was reported by Sterling and Swann in 1965for depositing a-Si, SiO2 and Si3N4 films. This process also achieved industrial acceptance in the preparation of Si3N4 films. Also Reference No.329 Swann, Mehta and Cauge.
2013 SEPT	Kebaili, H O K Faculte Des Sciences et Technologie Universite Kasdi Merbah, Ouargla, Algeria	Contribution à L'étude par la simulation numerique de Dynamique Moléculaire de la croissance des couches minces par procédé PECVD	MSc Thesis 17/09/13	Le Dépôt Chemique en phase vapeur assisté par plasma (PECVD) (Plasma Enhanced Chemical Vapor Deposition) est l'une des technique de CVD qui permet de déposer des couches minces homogènes; uniformer de materiaux divers (polymères, céramique, hybrides), elle fût inventee par Sterling et Swann.
2013 AUG	Zatirostami A Etal Islamic Azad University, Sari, Iran	Probing the Nature of Annealing Silicon Carbide Samples for Solar Cells	Journal of Applied Chemical Research 7, 4, 7 -13 (2013) 34th Aug. 2013	Today, nano-materials and nano structures are not only the forefront of the hot researches on the fundamental material, but have also entered slowly and in-obtrusively into our daily lives. In recent years, the dye-sensitised solar cells (DNSC) based on nano structure metal oxide films have attracted much attention to themselves. The electrons and holes produced by light on a shorted path to prevent the charge recombination greatly. Ref. 1+2 Sterling and Swann.
2013 JUNE	Kim Y Kyushu University Fukuoka Japan	Effects of Si Cluster Incorporation on a-Si:H/uC-Si:H Films Deposited by Plasma Chemical Vapor Deposition	Thesis 06/2013	Passivation of dangling bonds is therefore necessary to improve the electrical features of the material. In that sense, dangling bonds can be passivated by the addition of hydrogen during the deposition process, thus leading to the well known a-Si:H, whose electrical properties permit its use in solar cell technology Ref. Sterling and Swann
2013 JUNE	Maslova, Olga Université Paris-Sud Laboratoire de Génie Électrique de Paris . France	Capacitance spectroscopy in hydrogenated amorphous silicon schotky diodes and high efficiency heterojunction solar cells	PhD Thesis	In 1965 it was discovered that deposition of amorphous silicon employing glow discharge in the deposition technique yielded a material with much more useful electronic properties {Ref. Sterling and Swann}

2013 MAY	Pradhan P. National Institute of Technology, Rourkela, Orissa, India	Growth and Characterizationo f Silicon Nitride thin film on Silicon Substrates	MSc Thesis	Another technique of significance is plasma enhanced CVD (PECVD), which uses plasma instead of thermal activation to impart the necessary energy for the reaction to occur and was first reported in 1965 by Sterling and Swann for the deposition of amorphous silicon, SiO2 and Si3N4.
2013 APRIL	Boulesbaa, M. Faculté de Technologie Université Hadj Lakhdar de Batna, Algeria	To be confirmed	DSc Thesis 27-04-13	P9. 3.1 Technique de dépôt des films minces. Afin d'abaisser la temperature d'élaboration des films dans les procèdes CVD, Sterling et Swann out invente la nouvelle technique PECVD datee depuis 1965 [29] - Sterling and Swann. Cette technique est basee sur le fact d'un plasma qui constitue de plusieurs espèces comme les électrons, les ions, les radicaux et les atomes excites.
2013 JAN	Minne de Jong Universiteit Utrecht, Holland	Light Trapping in Thin Film Solar Cells on Plastic Substrates	Proefschrif t Thesis	In 1965,Sterling (and Swann) showed the possibility to deposit a-Si:H in a radio frequency (RF) discharge.
2013	Boszkowicz, P Akademia G H University of Science and Technology Krakow, Poland	Krzemowe warstwy funkejonalne na ogniwa sloneczne	PhD Thesis	1.3.3 Krzem amorficzny I warstwy a-Si:H Pierwsze warstwy amorficznego krzemu otrz ymano w 1965 r., pod nazwa "silicon from silane" (Ref.Sterling and Swann)
2013	Menendez A. Sanchez P Gomez D. Energy Area, ITMA Materials Tech'y, Parque Empresarial P.E.P.A. Aviles, (Asturias) Spain	Deposition of thin films: PECVD Process. Chapter 2 Pages 29 - 57	Depositio n of thin films: PECVD Process. Chapter 2 Pages 29 - 57 Depositio n of thin films: PECVD Process. Chapter 2 Pages 29 - 57	3.0 Plasma Enhanced Chemical Plasma Deposition. Today, silicon based thin film solar cell is a well established technology and must be taken into account in the race to achieve the important goal of cost reduction of photovoltaic devices. First hydrogenated amorphous silicon (a-Si (H)) devices were carried out by Sterling and Swann and Spear and Lecomber using a reactor with a silane (SiH4) glow discharge induced by radio frequency (RF) voltages, etc.3.0 Plasma Enhanced Chemical Plasma Deposition. Today, silicon based thin film solar cell is a well established technology and must be taken into account in the race to achieve the important goal of cost reduction of photovoltaic devices. First hydrogenated amorphous silicon (a-Si (H)) devices were carried out by Sterling and Swann and Spear and Lecomber using a reactor with a silane (SiH4) glow discharge induced by radio frequency (RF) voltages, etc.

2012 SEPT	CHEN W. Kyushu University, Fukuoka Japan Graduate School of Engineering Science	Study on VHF Plasma Characteristics by Laser Thomson Scattering	PhD Thesis	2.1 Overview of Solar Cells. Sterling and Swann were the first to publish the formation of films of "silicon from silane" in a radio frequency glow discharge in 1965
2012 AUG	SiNAPS Report – Coordinated by Tyndall National, Institute, Cork, Ireland.	Semiconducting Nanowire Platform for Autonomous Sensors	SiNAPS Report D1.6 REV. 1.0 Co-Funded by European Commissi on	Amorphous silicon (a-Si) and hydrogenated amorphous silicon (a-Si:H) are model amorphous covalent materials and are technologically important materials for photovoltaic applications [1]. The so-called second generation solar cells are constructed from a-Si thin films Ref. Sterling and Swann
2012 MAY	Meerwijk J. Delft University of Technology Holland	Analysis of Electronic transport in HIT Solar Cells	MSc Thesis	Amorphous silicon has been of particular interest to the electronic industry since 1965 when Sterling and Swann reported the deposition of amorphous silicon onto a substrate
2012 APRIL	Halim M. M. Carnegie Laboratory of Physics University of Dundee, Nethergate Scotland	Physical Characteristics of Laser Processed hydrogenated amorphous Silicon	PhD Thesis	The first report on amorphous silicon deposition using silane gas was successfully made by Sterling and Swann. Ref. Solid State Electronics, 8, 653 (1965)
2012	Budini N. Instituto de Desarrollo Tecnologico Para la Industria Quimico, Universidad Nacional de Litoral Bogota, Colombo	Silicio Policristalino Para Dispostivos Fotovoltaicos	PhD Thesis	Silicio Amorpho. El a-Si fue depositado por primera vez por Sterling and Swann en el ano 1965, y subsecuentement Chittick et al, fueron las primeros que lograron una calidad razonable de las películas depositadas por el método de deposición quimíca desde la fase vapor asistida por plasma (plasma-enhanced chemical vapor deposition, PECVD). La gran ventaja que introdujo este material es la posibilidad de depositarlo a temperaturas bajas, en el orden de los 200 deg.C, que permiten utilizar sustratos más económicos como es el caso del vidrio.

2012	Coyle C. Dublin City University, Ireland	Investigation of Plasma Processes in Surface Modification with Biodiagnostic Applications	PhD Thesis	The 1960s saw the first studies of surface modification using plasma assisted processes (Ref. Sterling and Swann) which focused on protective coatings and surface activation. It is expected that the use of plasma processes will continue to expand because they have unique capability, are economically attractive and are friendly towards the environment.
2011 OCT	Schuttauf J.W.A. University of Utrecht Holland	Amorphous and Crystalline silicon based heterojunction solar cells	PhD Thesis ISBN: 178-90-393-5641-8	In 1965, it was discovered, by Sterling and Swann, that a-Si:H deposited by the glow discharge technique – using plasma, also known as Plasma Enhanced Chemical vapor Deposition (PECVD) – reduced the defect density of the material even further. In 1976, the first a-Si:H based thin film solar cell was fabricated at RCA Laboratories.
2011 OCT	Katzel J. Brandenburgische Technische Universitat Cottbus Germany	Technologiestudie zur Herstellung von Silizium-Dunnschichtsolarzellung	Bachelorarbeit	Ref. Sterling and Swann
2011 AUG	Katzer D S Meyer D J Et al, Naval Research Laboratory, Overlook Ave., Washington, DC. USA	Ultra=High Vacuum Deposition and Characterisation of Silicon Nitride Thin Film Page 71	Presented at 28th N.A. Molecular Beam Epitaxy Conference (NAMBE) San Diego University, California	Thin Films of silicon nitride (SiN) dielectric material have been used in microelectronics for decades - one of the earliest reports was from 1965. Ref. Sterling and Swann. This important material has been used in a variety of applications including passivation layers for Group 111 nitride (111-N) HEMTS {2} and integrated circuits, gate dielectrics in field effect transistors and diffusion barriers.
2011 JUNE	Lu J. University of Twente, Holland	Solar Cells on CMOS Chips as Energy Harvesters ISBN 978-90-365-3211-2	PhD Thesis	In 1965, Sterling and Swann found that Si, SiO_2 and Si_3N_4 layers can be deposited by chemical vapor deposition (CVD) promoted by radio frequency discharge of silane containing gases

2011 MAY	Flannery A.F. Stanford University Palo Alto California USA	Fabrication methods for Enviromentally Hardened Sensors	PhD Thesis (Pages displayed by permission of Stanford University) Available by Google Books	Chapter 1 Development of a Chemically Robust Dielectric. Before pressing forward into the study of PECVD silicon carbide it is worth reviewing the history of the material. Before methods of controlled plasma deposition were developed, amorphous silicon carbide was deposited by pyrolytic methods which relied on the combustion of reactants to generate the desired product [10] The earliest reference to the deposition of silicon carbide by radio frequency plasma was by Sterling and Swann [11]. At this time, PECVD deposition was referred to as the glow discharge method of deposition
2011	Remache L. Departement D'Électronique Université Mentouri-Constantine Algeria	Silicium Poreux Passivé par des nitrures et des oxides de silicium. Application aux revêtements anti réfléchissants.	DSc Thesis	Le Dépôt chimique en phaseée vapeur assisté par plasma. Inventée en 1965 par Sterling et Swann[1] la technique PECVD fut appliqués à l'industrie photovoltaique à partir du milieu des années 1970 pour réalization de cellules en silicium amorphe.
2011	Wordenweber J. RWTH Aachen University, Aachen Germany	Impact of contamination on hydrogenated amorphous silicon.	PhD Thesis Published in Schriften des Forschungzentrum Julich. Energy & Environment ISBN 978-3-89336-697-2 2011	This study deals with amorphous (a-Si:H) and monocrystalline (uc=Si:H) hydrogenated silicon thin film solar cells. The concept of a-Si:H solar cells was first reported in 1965 by Sterling and Swann
2011	Espinosa D.H.G, Escola Politecnica da Universidade de Sao Paulo, Brazil	Efeito de lente termica e Nao-linearidades opticas do solicio amorfo hidrogenado dopado com fosforo	Masters Thesis	Os primeros trabalhas a apresentarum tecnicas de obtencao do solicio amorfa hidrogenado a partir de gas silana por deposicao quimica na fase vapor, atraves de uma descargo luminescente, form realizados por Sterling and Swann (1968) sic 1965.
2011	Tozlu N. Cukurova Universitesi Fen Bilimleri Enstitusu, Adana Turkey	Investigation of Metal Contact Properties at ZnO based semiconductors	MSc Thesis	3. Materyal ve Metod 1965 te Sterling ve Swann, plasmalarm CVD dekompozisyonnundaki onemi hakkinda tartistilar. Genellikle plazma ile biriktirme yapilirken, molekuller tam olarak ayrismaz, bu durumda molekullerin spektrum duzeninin ve molekuler parcalarinin notr ve iyonize olmasini sagla. Plazma ayrismasi ve buhar fazi nukleonlanmasi, super ince partikuller uretilmesini saglayabilmektedir.

2010 DEC	Wassila D. Mme. Université Abou Bekr Belkid de Tlemcen, Algeria	Modelisation des Structures Photovoltaiques : Aspects Fondamentaux et Appliqués	PhD Thesis 19/12/2010	Dans I'industrie photo-voltaíque, la technique la plus répondue pour êlaborer les couche minces de nitrure de silicium est le dépôt chemique en phase vapeur (CVD – Chemical Vapor Deposition) assisté par plasma (PECVD – Plasma Enhanced Vapor Deposition) à partir des gaz silane (SiH4) et amoniac (NH3) Cette technologie permet de réalizes des dépôt assiste pat plasma à été invente en 1965 par Sterling and Swann et initialement utilisé dans le domaine de la microeléctronique.
2010 SEPT	Bakker R. Physics of Devices sub group University of Utrecht Holland	Hot-wire chemical vapour deposition at low temperatures for Optoelectronic Application	PhD Thesis ISBN 978-90-393-5395-0	In the early 1960s, the first papers mentioning the term "chemical vapour deposition"were published.. These were deposition of tungsten films from WF6 on a heated substrate. Soon after that, deposition of silicon, silicon oxide (SiOx) and silicon nitride (SiNx) with the use of a radio frequent (sic) frequency discharge (or plasma) was Published (Ref. Sterling and Swann).
2010 AUG	Hameiri Z. Centre for Photovoltaic Engineering TheUniversity of New South Wales,Sydney Australia	Laser Doped Selective Emitter and Local Back Surface Field Solar Cells with Rear Passivation	PhD Thesis	Reference
2010 JULY	Woo G.P. Department of Electrical Engineering, National Chung Hsing University Taiwan	Study in the Fabrication of Hydrogenated Amorphous Silicon Films using VHF-PECVD for thin film solar cell.	MSc Thesis	Reference to Sterling and Swann under heading:1.2: 'Motivation and Purpose'
2010 JULY	Lee C-Y Tatung University, Taipei Taiwan	The development of Low Temperature and High Speed Deposition of Crystalline Silicon Films	MSc Thesis	The amorphous silicon thin film was first made by Sterling and Swann in 1965 by using RF glow discharge to decompose the silane (SiH4) to produce the amorphous silicon thin film.

2010 JUNE	Fazia N.K. Université M'Hamed Bougara – Boumerdes Algeria	Étude et réalization de couches d'oxynitrure de silicium sur un substrat de silicium monocristallin ou multi cristallin	Memoire de Magister 27/06/2010	III. 1. 1 Dépöt assisté par plasma (PECVD) Inventée en 1965 par Sterling and Swann et Initialement utilisée dans la domaine de la microélectronique, la technique PECVD fut ensuite l'industrie photo-voltaïque à partir du milieu des années 1970 pour la réalization de cellules en silicium amorphe. Depuis, de nombreuses recherches ont été menées au sein de laboratories universitaires et industriels pour optimizer celle technique de dépôt.
2010 APRIL	Holschwandner L. and Rana V. Agere Systems, Orlando, Fla. USA	Tungsten Metallization	US Patent 5,227,335 C1 Ex Parte Reexamination Certificate	Ref. US Patent 3,655,438 Sterling et al and Swann et al Jnl. Electrochem. Soc. July 1967 pp 713-717
2010 JAN	Yu G.Z. Dept. of Electr. Eng. National Chung Hsing University, Taichung, Taiwan	Study in the Fabrication of Hydrogenated Amorphous Silicon using VHF - PECVD for thin film solar cell.	MSc Thesis 108 Pages	Ref [2] Sterling and Swann. No translation available.
2010	Azizur Rahman K.M. University of Waterloo, Ontario Canada	Nanocrystalline Silicon Solar Cells Deposited via Pulsed PECVD at 150 deg.C Substrate Temperature	MSc Thesis	Nc-Si:H evolved out of the continuous research activity on a-Si:H. H.F. Sterling and R.C.G. Swann (1965), were the first to report a-Si:H thin film following the radio frequency (rf) Plasma Enhanced Chemical Deposition (PECVD) process [4] Sic.
2009 DEC	Gorin A. Université De Sherbrooke, Quebec, Canada	Réalisation de guides d'onde plans faibles pertes en nitrure de silicium pour un biocapteur intègre	PhD Thesis ISBN 978-0-494-62822-5	Chapitre 4 Dépôt and Characterisation du nitrure de silicium pour la Propagation du champ evanescent. La premiere fois utilisée en 1965 pour la passivation de circuits microélectroniques en silicium. Ref Sterling and Swann 1965

2009 NOV	Dupuis J. L'Institut National des Sciences Appliquées de Lyon France	Élaboration et characterisation de couches de SiOx Ny:H et SiNx:H realisees par methode PECVD.. Photovoltaiques en silicium	PhD Thesis	Inventee en 1965 par Sterling et Swann la technique PECVD fut appliqué a industrie photovoltaique ….
2009 OCT	Zhu F. and Madan A. MV Systems, Golden CO. and Department of Physics, Golden Colorado School of Mines,Golden, Colorado. Also, Gaillard and Miller, University of Hawaii at Manoa, Honolulu, USA	Amorphous silicon carbide photoelectrode for hydrogen production directly from water using sunlight	Philosophical Magazine Vol. 89 Oct. 2009	Amorphous silicon (a-Si) is the basis of a multi-billion dollar industry in applications as diverse as active matrix liquid crystal displays (AMLCD). Electro-photography, image sensors, solar cells, etc. The origins of this remarkable commercial success can be traced to the work at Standard Telephone(sic), Telecommunications Laboratories (STL), Harlow, UK 1965 [ref. Sterling and Swann].
2009 JUNE	Olumide A.K. Laboratory of Photovoltaic Materials and Devices, Delft University of Technology Holland	Investigation of the relation between growth mechanism and material properties of amorphous silicon solar cells.	MSc Thesis	The first deposition of hydrogenated amorphous silicon (a-Si:H) was reported by Sterling and Swann and also by Chittick et al. They deposited a-Si:H) from a silane (SiH_4) gas in a radio frequency glow discharge .

2009 JUNE	Gloger S. Am Facbereich Physik der Universitat Konstanz Germany	Verbesserte Ruckseitenpassivierung siebgedruckten Bifacialen Silizium Solarzellen	Diplomararbeit June 2009	Die chemische gasphasenabscheidung bei vermindertem druck (low pressure chemical vapor eposition,LPCVD) Aus dichlorosilan ($SiH_2 Cl_2$) und ammoniak bei temperaturen von 700 bis 800 Deg.C. Ref. Swann, Mehta, unt 2 Grundlagen der Silizium Solarzelle. Die plasmaktivierte chemische Gasphasenabscheidung vapor deposition (PECVD) von Silan und Ammoniak / Stickstoff – Gemischen bei temperaturenunter 500 deg.C reduziertem druck Ref. Sterling and Swann
2009 MAR	Mirkhlif H M. Dept. of Physics, Al-Mustansiriya University, Baghdad, Iran	Illumination and Dark Current Voltage Characteristics of Polymer-Silicon Hetero-Junction S0lar Cells	IJAP Letters, Vol.2 No. 1 Jan-Mar 2009	The beginning of amorphous silicon voltaics (PV) goes back to 1965, when Sterling and Swann (2) reported deposition of silicon onto a substrate using a silane glow discharge
2009 JAN	Li C. New Jersey Institute of Technology, New Jersey University, Newark, New Jersey, USA	Surface and Bulk Protection of Multicrystalline Silicon Solar Cells by silicon nitride (H) layer: Modeling and Experiments	PhD Thesis	The first publication specifically aimed at plasma-enhanced deposition for semiconductor processing appeared in 1963 by L.L. Alt etal Jnl. Electro. Chem. Soc. 110, 465 (1963) Two years later, PECVD technique was invented by Sterling and Swann. This technique was soon utilized in IC technology and, in the mid 1970s, in photo voltaic (PV) technology when the first PECVD amorphous silicon (a-Si) thin film solar cell wasfabricated in RCA Laboratories by Carlson and Wronski in 1976.
2009 JAN	Mikhlif H M Dept. of Physics. College of Science, Al-Mustansiriya University, Bagdad, Iraq	Illumination and Dark Current-Voltage Characteristics of Polymer-Silicon Heterojunction Solar Cells	Iraqi Journal of Applied Physics Letters IJAP Lett. Vol.2. No 1 Jan-Mar 2009	The beginning of amorphous-silicon photovoltaics (PV) goes back to 1965, when Sterling and Swann reported deposition of silicon onto a substrate using a silane glow discharge.

2009	Fernandes, Luis M T Universidade Nova De Lisboa Faculdade de Ciencias Technogia Lisbon, Portugal	Sesores de Imagem de Grande Area em Technologia de Silicio Amorfo	Thesis DSc	**2.2 Silicio amorfo hidrogenado** A possibilildade de passivacao dos defeitos pela introducao de hidrogenio durante o processo de fabrico por deposicao quimica de vapor assistida por plssma (PECVD) veio fornecer o impulso que faltava a este tipo de material. Embora estejam documentadas desde 1965 tentativas nesta direccao (Sterling and Swann)
2008 DEC	Zeeman N Et al Delft University of Technology, Holland And Sutta P University of West Bohemia Pilsen Czech Republich	Structural Properties of amorphous silicon prepared from hydrogen diluted silane	Published in The Philosophical Magazine and Letters 19th Dec 2008	The first amorphous silicon layers were reported in 1965 of' silicon from silane' deposited in a radio frequency glow discharge (1) Ref. Sterling and Swann
2008 DEC	Amtablian S. L'Institut National Des Sciences Appliquees De Lyon France	Du transfert de films minces de silizium monocrystallin vers un procédé cellule à faible budget thermique	PhD Thesis	1.3.2.1.2 Procédé de dépôt Historiquement, le premier dépôt de silicium amorphe a été réalisé dans un réacteur PECVD radio fréquence (ref. Sterling and Swann). C'est aujourd'hui la méthode la plus communément utilisée avec une fréquence du plasma 13.56 MHz. Le silane (SiH_4) est dissocié dans un plasma d'argon et d'hydrogene a une temperature inférieure à 250 deg. C.
2008 OCT	Bhaduri A. Energy Research Unit Indian Assoc'n for the Cultivation of Science Jadavpur University Kolkata India	Structural Studies of Silicon, Germanium, Carbon Alloy Thin Films	PhD Thesis	Deposition of hydrogenated amorphous silicon (a-Si:H) was first reported by Sterling and Swann.

2008 APR	Leal-Cruz A.L. etal IPN-Unidad Saltillo, Coahuila, Mexico	A Low Temperature and seedless method for producing hydrogen-free Si3N4	Revista Mexicana De Fisica 54 (3) 200 – 207	The synthesis of both amorphous and crystalline Si3N4 has been extensively investigated for opto-electronic and microelectronic applications [13 etc] R.C.G. Swann, R.R. Mehta and T. P. Cauge.
2008 FEB	Giazotto F. Heikkila T.T. et al Helsinki University of Technology, Low Temp. Laboratory. Helsinki, Finland	Thermal Properties in mesoscopics: Physics and Applications from thermometry to refrigeration	Google xxx.tau.ac.il/pdf/cond-mat/0508093	Page 48 D. Thin film insulators. Silicon nitride is another insulating film that forms good interfaces with Si. It is nowadays successfully used as interlevel dielectric (Swan (n) et al., 1967).
2008 FEB	Zeyrek S. etal Dunlupinar University 43100 Kutahya Turkey	Analysis of formation of silicon nitride on Si (100) by electrochemical anodization	AKU Fen Bilimleri Dergisi 2008-02 21 – 25	Since it was first reported in 1965 by Sterling and Swann that silicon nitride (Si3N4) could be used as surface passivation films in integrated circuits (IC), silicon nitride films, in particular, have been widely used in IC processing as dual dielectric gate films, local oxidation masks and surface passivation films due to their superior electronic properties such as high dielectric constant, stability and strong resistance to diffusion.
2008	Shin K-W University of Waterloo Ontario, Canada	Fabrication and Analysis of Bottom Gate NanoCrystalline Silicon Thin Film Transistors	MSc Thesis	Sterling and Swann were the first to use plasma enhanced chemical vapor deposition (PECVD) to grow a-Si:H and amorphous silicon nitride (a-SiN) from silane (SiH4) gas in 1965. The use of silane caused hydrogen to be incorporated in films and they passivated dangling bond defects leading (to) better quality material. Sanyo first commercialized calculators powered by a-Si:H solar cells in 1979.
2007 DEC	Klaver A. Technische Universiteit Delft Holland	Irradiation Induced Degradation of Amorphous Silicon Solar Cells in Space	PhD Thesis ISBN 978-90-9022469-5	Thin film(s) of a-Si:H can be deposited using plasma-enhanced chemical vapor deposition using silane gas (SiH4) as the precursor ref. Sterling and Swann.

2007 JULY	Alcantara S.P. Institute of Solar Energy Universidad Politecnica de Madrid Spain	Fabricacion de celulas solares sobresilicio multicristalino y silicio purificado por la via metalurgica	PhD Thesis Chapter 5 Deposito de capas de nitruro de silicio por PECVD	El metodo de deposito quimico en fase do vapor potenciado por plasma (Plasma Enhanced Chemical Vapor Deposition PECVD), se invento por los fisicos Sterling y Swann el ano 1965. En sus inicios se empleo en dispositivos electronicos, reduciendo la necesidad de utilizar el oxido de silicio.
2007 JULY	Ren S.J. Dept of Materials Eng. Tatung University, Taipei, Taiwan	Influence of modulated RF silane plasma on the gap states and stability of the intrinsic layer of a-Si:H Solar Cell.	Msc Thesis Approved 26th July 2007	1965 Ref. Sterling and Swann (Text only in Chinese)
2007 APRIL	Lelievre J-F L'Institut National de Sciences Appliquées de Lyon, France	Élaboration de SiNx:H par PECVD: Optimisation des propriétés optiques, passivantes et structurales pour applications photovoltaïques	PhD Thesis	Chapter11 Clause 1.2 P44 Dépôt assisté par plasma (PECVD) Inventée en 1965 par Sterling and Swann [69] et initialement utilisée dans le domaine de la microélectronique, la technique PECVD fut ensuite appliquée à l'industrie photovoltaïque a partir du milieu des année 1970 pour la réalisation de cellules en silicium amorphe.
2007	Mates T. etal Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnicka 10, Prague Czech Republic	Structure of mixed-phase Si films studied by C-AFM and X-TEM	IOP Publishing doi:10 . 1088/1742-6596/61 /1/158	The samples presented in this work were prepared by plasma enhanced chemical vapor deposition (PECVD) (Ref. Sterling and Swann) at very low deposition temperature of Ts= 39deg. C

2007	Neuhaus D-H Etal Deutche Cell GmbH, Freiberg Germany	Review Article: Industrial Silicon Wafer Solar Cells	Hindawi Publishing Corporation Advances in Microelectronics. Vol.2007 Doi: 10.1155/2007/24521	Today, plasma-enhanced chemical vapor deposition (PECVD) is most widely used in the photovoltaic industry to deposit SiNx:H as an anti reflection coating. The PECVD method was invented in the field of microelectronics by Sterling and Swann in 1965. In 1981 the method was first applied to solar cells by Hezel and Schorner. Kyocera in Japan was the first company that used the PECVD method commercially for screen printed multicrystalline silicon solar cells achieving good optical properties as well as good surface and bulk passivation.
2006 OCT	Poortmann J. (IMEC, Leuven, Belgium) and Arkhipov V. formerly Institut of Physics and Enginering. Moscow and IMEC	Thin Film Solar Cells Fabrication, Characterisation and Application. Advanced Amorphous Silicon Solar Cell Technology Chapter 5 by Prof. Miro Zeman, Delft University of Technology	Wiley & Sons 1st Edition 2006 ISBN-10-0470-09126-6 (HB)	The first amorphous silicon layers were deposited in a radio frequency driven glow discharge using silane. (Ref. Sterling and Swann, 1965). The radio frequency glow discharge method, today known as PECVD, is still the method most commonly used, both in the laboratory and on an industrial scale.
2006 OCT	Kramer M. C.J.C.M. Technische Universeit, Eindhoven, Holland	Gallium Nitride-based Microwave High-Power Heterostructure Field Effect Transistor	PhD Thesis	Already in 1965, Sterling and Swann described SiN deposition by PECVD
2006 SEPT	Aarts I.M.P. Technische Universiteit Eindhoven Holland	Optical Probing of Dangling Bonds During Thin Film Growth.	PhD Thesis 21st September 2006	Hydrogenated amorphous silicon with good opto-electronic properties was first deposited from a silane (SiH4) glow discharge in the 1960's by Sterling and Swann [1], and Chittick et al. From the beginning the research has been focused on the a-Si:H material properties, especially the role of hydrogen, substitutional doping and the plasma decomposition of the precursor gases were studied.

2006 MAY	Mates T. Charles University, Faculty of Mathematics and Physics, Prague, Czech Republic	Structure and Properties of thin film silicon films for solar cells	PhD Thesis	The Plasma Enhanced Chemical Vapor Deposition (PECVD), based on decomposition of a source gas containing silicon by means of a plasma. This method (was) first reported by Sterling and Swann in 1965
2006 APRIL	Madan A. MV Systems Inc. Golden Colorado USA	Amorphous silicon- From doping to multibillion dollar applications	Jnl. of Non Crystalline Solids Elsevier 24th April 2006	The origin of this remarkable commercialisation success can be traced to the work at Standard Telephone (Sic) Labs (STL) Harlow UK (1965 - 1969). 2. a-Si work at STL England. The work on a-Si using the electrodeless glow discharge (now referred to as PECVD) in silane gas (SiH4) was pioneered by Sterling and his co-workers at STL starting in 1965 (Sterling and Swann)
2006 FEB	Schwartz G. Ex IBM Srikrishnan K. V. IBM	Interlevel Dielectrics by Geraldine Schwartz and K. V. Srikrishnan	Handbook of Semiconductor Interconnection Technology 2nd Ed. Feb. 2nd Published by Taylor and Francis Gp. 507 Pages	PECVD nitride was first reported by Sterling ands Swann (1965) who prepared it from SiH4 and NH3 in a tubular reactor. As Sterling and Swann pointed out, N2O is preferred over O2 because of the spontaneous reaction between SiH4 and O2 4.2.4.1 Capacitively Coupled Plasmas; Bell jar reactors SiH4 and N2O were used by Sterling and Swann (1965) who found that, although films can be formed at low temperature, they contained a large amount of water. Higher deposition temperatures were preferable, the films formed were hard, glossy and adherent.
2006	Tetsuo Soga (Editor) Nagoya Institute of Technology, Nagoya, Japan	NonStructered Materials for Solar Energy Conversion. Chapter 5 Page 142 by Schropp R.E.I.	Elsevier ISBN-13: 978-0-444-52844-S	The first amorphous silicon layers were deposited in a rf driven glow discharge using silane, ref. Sterling and Swann, now usually called PECVD. PECVD has become the workhorse of the thin film semiconductor industry and is generally used for the deposition of thin film solar cells.
2006	2006	Non Structured Materials for Solar Energy Conversion. Chapter 5 Page 142 by Schropp R.E.I.	Elsevier ISBN-13: 978-0-444-52844-S	The first amorphous silicon layers were deposited in a rf driven glow discharge using silane, ref. Sterling and Swann, now usually called PECVD. PECVD has become the workhorse of the thin film semiconductor industry and is generally used for the deposition of thin film solar cells, etc.

2005 OCT	Veneri P D The Italian Agency for New Technologies, Energy and Sustainable Economic Growth, ENEA Research Centre, Portici, Italy	Thin Film Silicon Solar Cells	Presentation on Oct 17-29th 2005 at a workshop on Physics for Renewable Energy. The Abdus Salam Int. Centre for Theoretical Physics	The unique properties of amorphous and microcrystalline silicon, together with the modern technique for preparing thin films over large areas, opens many opportunities for semiconductor applications. 1965: Sterling and Swann report the formation of films of "silicon from silane" in a radio frequency glow discharge.
2005 SEPT	Sparrow I J G Opto-Electronic Research Centre University of Southampton England	Development and application of U.V. written waveguides	PhD Thesis	The possibility of using a plasma to assist chemical vapour deposition has been known for many years. Thin films of silica deposited using silane and nitrous oxide (the precursors that form the basis of the work in Chapter 6 (of this thesis) were deposited with plasma assistance in the mid 1960s Ref. Sterling and Swann, onto silicon substrates.
2005 MAR	Smit Chiel Technical University Eindhoven Holland	Expanding Thermal Plasma Deposition of Microcrystalline Silicon for Solar Cells	PhD Thesis	The history of thin film silicon starts with the development of hydrogenated amorphous silicon (a-Si:H) by Sterling and Swann and later by Chittick etal 1969.
2005 FEB	Bakardjieva K etal Central Laboratory for Solar Energy, Institute of Solid State Physics, BAS Sofia, Bulgaria	Effect of Rapid Annealing on the Properties of uPVCD and PECVD silicon nitride thin films	Journal of Optoelectronics and Advanced Materials Vol. 7 No. 1 Feb 2005 PP 377-380	Plasma enhanced CVD (PECVD) is carried out below 400 deg. C., and uses an electrical discharge to decompose the chemical precursors (Ref. Sterling and Swann)
2004 MAR	Korevaar B.A. Eindhoven University of Technology Holland	Integration of Expanding Thermal Plasma deposited by Hydrogenated amorphous silicon in solar cells	Proefschrift Thesis	Deposition of hydrogenated amorphous silicon (a-Si:H) was first reported by Sterling and Swann

2004 JAN	Mattox D.M. 'Management Plus, Inc.' Albuqueque, New Mexico USA	The Foundations of Vacuum Coating Technology	Noyes / William Andrew ISBN-0-8 155-1495 -6 150 pages	In 1965 Sterling and Swann discussed the importance of plasmas in decomposition of chemical vapor precursors. When depositing species from a plasma, the molecules are often incompletely disassociated thus forming a spectrum of molecules and molecular fragments, both neutral and ionized.
2004	Carabe J. etal CIEMAT. 22 Madrid Spain	Thin-Film-Silicon Solar Cells	Opto-Electronic s Review 12 (1) 1-6 2004	The beginning of amorphous-silicon PV goes back to 1965, when Sterling and Swann reported deposition of silicon onto a substrate using a silane glow discharge.
2004	Grant D. J. University of Waterloo, Ontario Canada	Bottom-Gate TFTs with Channel Layer Deposited by Pulsed PECVD	MSc Thesis	Sterling and Swann were the first to use PECVD to grow a-Si:H (as well as silicon oxide (SiO) and amorphous silicon nitride (a-SiN:H) from silane (SiH4) gas in 1965.
2004	Mohamed E Murdoch University, Perth, Western Australia	Monocrystalline Silicon Thin Films Prepared by Hot-Wire Chemical Vapour Deposition	PhD Thesis	A large variety of methods are used for the fabrication of thin films, such as Very High Frequency Chemical Vapour Deposition (VHF-CVD) [Ishikawa et al 1987], Plasma Beam Deposition (PBD) [Koynov et al 1994], layer by layer technique [Ishihara et al 1993] and chemical annealing [Shirai et al 1991] however the most commonly used are Plasma Enhanced (PECVD) [Sterling and Swann 1965] and Hot-Wire CVD (HW-CVD) [Wwismann et al 1979]
2004	Arft C. M. University of California, Davis, California USA	Chemistry of Silicon Oxynitride Deposition	PhD Thesis	The earliest reported PECVD (although it was not called such at the time) deposition of oxynitride from silane and nitrous oxide was given by Sterling and Swann in 1965. They obtained fairly high deposition rates (30 – 60 nm/min) at temperatures ranging from room temperature to 500 deg.C. They found that the deposited films were amorphous with absorption spectra different from that of standard silica or quartz. Etc.
2003 NOV	Kushner M.J. University of Illinois Urbana Illinois USA	Continuity in Plasma Processing: Yesterday's Accomplishments, Today's Innovations, Tomorrows Challenges	Work supported by: SRC, NSF, Sematech, GE and EPRI	1790's First Glow Discharges (Hawksbee) 1830's Glow Discharges M. Faraday). 1890's RF Discharges (N. Tesla). 1900's Transport (J.S. Townsend). 1960's PECVD (Sterling and Swann).

2003 OCT	Salabas A. Instituto Superior Tecnico. Universidade Tecnica de Lisboa, Portugal	Fluid Model for Charged Particle Transport in capacitively coupled Radio Frequency Discharges	PhD Thesis	Hydrogenated amorphous silicon films have been reported in the works of Sterling and Swann 1965 and Chittick et al 1969, where the passivation of dangling bonds by hydrogen was observed,
2003 MAY	Awan S.A. etal School of Chemistry and Physics Keele University Staffs. England	Electrical properties of Nitrogen RF-Sputtered Silicon Nitride Thin Films:Effects of Gold Electrodes	Acta physica Slovaca Vol. 53 No.5, 347 - 358	Values of relative permittivy in the range of 7 – 11 were found for films prepared using a glow discharge Reference Swann, Mehta and Cauge J. Electrochem. Soc: Solid Statee Sci. 114 (1967) 713
2003	Salyk O. Inst. of Physical and Applied Chemistry, Brno University Czech Rep.	Thin Film Deposition of Amorphous Silicon and Organosilicon Compounds	Post Doctorate Thesis (Habbilita tion)	The a-Si:H thin films of device quality was first prepared by decomposition of silane in 1965 by Stearling (sic) and Swann (1) through a radio frequency glow discharge in SiH4.
2003	Mattox D.M. Society of Vacuum Coaters Albuerquerque New Mexico USA	Historical Timeline of Vacuum Coating and Vacuum/Plasma Technology	Copyright 2003 - 2012	1678 - Picard's glow (plasma). ~1720 - Electrical (glow) discharge generated (Hawksbee). 1885 – Inductively excited plasmas (Hittorf). 1921 – Plasma desorption from surfaces (Campbell). 1965 - Plasma enhanced CVD (Sterling and Swann)
2003	Boshta M. (Egyptian) Physikalisches Institut George-August – Universitat zu Gottingen Germany	Characterisation of Hydrogenated Silicon Thin Films and its Alloys by the photoconductivi ty frequency mixing and transient thermoelectric effects method	PhD Thesis	Amorphous and polycrystalline thin films are still produced using the method that first resulted in hydrogen incorporation in the material (Ref. Sterling and Swann). The deposition method is a glow discharge technique also known as Plasma Enhanced Chemical vapor Deposition (PECVD). A silicon containing gas, usually silane (SiH4), is admitted to a vacuum reactor chamber. A gas discharge is then initiated and maintained by an electric field between two parallel plates' using either a d.c. voltage or a.c. voltage in the radio frequency domain (13.65 – 200MHz). The pressure is typically 0.1 – 1 mbar. Etc

2002 MAY	Kumar B. etal Tata BP Solar India	Commercialization of a Silicon Nitride Co-fire through (SINCOT) process for manufacturing high efficiency monocrystalline silicon solar cells	Paper presented at 29th IEEE PVSC New Orleans May 2002	Silicon Nitride (SiN) deposition by PECVD was invented in 1965 [Ref. Sterling and Swann]
2002 MAY	Smets A H M Technische Universiteit van Eindhoven Holland	Growth Related Material Properties of Hydrogenated Amorphous Silicon	Proefschrift Thesis ISBN 90-386-1969-3	The intrinsic a-Si:H films are deposited by means of silane containing plasmas, i.e. by means of plasma enhanced chemical vapour deposition (PECVD). The first reports on the deposition of a-Si:H material by means of a silane glow discharge, goes back to the 1960's Ref Ste65 Sterling and Swann and Chi69.
2002 JAN	Matsui T. Department of Physical Science Osaka University Japan	Material and Device Design for High Efficiency Polycrystalline Silicon Thin Film Solar Cells	PhD Thesis	In 1965. Sterling and Swann first published the deposition of amorphous silicon using silane (SiH4) in PECVD process.
2002	Narayanan S. BP Solar Frederick, Maryland USA	Large area multicrystalline silicon solar cells in high volume production environment – history, status, new processes, technology transfer issues	Elsevier Solar Energy Materials & Solar Cells 74 (2002) 107 - 115	SiN deposition by PECVD was invented in 1965 - Ref. Sterling and Swann. The SiN AR (anti-reflection) coating contains hydrogen, which diffuses during the metal contact firing and passivates bulk defects present in the wafer.
2002	Van Sark W.G.J.H.M. Debye Institute, Utrecht University Netherlands	Methods of Deposition of Hydrogenated Amorphous silicon for Device Applications	Academic Press Publications: 'Thin Films and Nanostructures' and 'Handbook of Thin Materials'	Chapter 4.3.4 'Plasma Enhanced Chemical Vapour Deposition' The possibility of using a plasma to assist chemical vapour deposition has been known for many years. Thin films of silica using silane and nitrous oxide (the precursor that forms the basis of this work of Chapter 6) were deposited with plasma assistance in the mid 1960s, ref.Sterling and Swann

2002	Van Sark W.G.J.H.M Debye Institute Utrecht University Netherlands	Methods of Depositionof Hydrogenated Amorphous Silicon for Device Applications	Academic Press Thin Films and Nanostructuresl. Vol. 30 ISBN 0-12-533030-8 2002	In 1965 it was discovered that deposition of amorphous silicon employing the glow discharge technique yielded a material with much more useful electronic properties (Ref. Sterling and Swann)
2001	Aberle A. G. University of New South Wales, Sydney Australia	Overview on SiN surface passivation of crystalline silicon solar cells	Elsevier Solar Energy Materials and Solar Cells 65 (2001) 239-248	Following the invention of the PECVD method by Stirling (sic) and Swann in 1965, this technique was soon used for electronic devices and in the mid-1970s, for photovoltaic (PV) devices… It appears that Kyocera in Japan was the first commercial user of plasma silicon nitride for c-Si solar cells.
2001	Gould R.D. etal Thin Films Laboratory, Keele University Staffs UK	DC conductivity in RF magnetron sputtered gold-silicon nitride-gold sandwich structures	Elsevier Thin Solid Films 398-399 (2001) 454-459	Silicon Nitride (Si3N4) is a particularly important film material in silicon and III/V device technology. Swann, Mehta and Cauge found relative permittivty values in the range 7 – 11 for films prepared using a glow discharge, while the bulk material values fell in a narrower range of 9 – 10.
2000 JAN	Rieve P. Universitat - Gesamthochschule Siegen, Germany	Spectralselective Optoelectronische Sensoren auf der Basis amorphen siliziums	PhD Thesis	2.1 Hydrogenisiertes, amorphes Silizium Den entsceidenden Durchbruch dieses Halbleitermaterials erlaubte die Möglichkeit der Hydrogenisierung des amorphen Siliziums während der Herstellung mit Hilfe eines plasmagestützten CVD Prozesses (PECVD), Plasma Enhanced Vapor Deposition). Obwohl bereits seit 1965 Versuche in dieser Richtung dokumentiert sind Sterling and Swann.
2000	Brummack H. Institut fur Physikalische Electronik der Universitat Stuttgart Germany	Optimierung von Driftbestimmten solarzellen aus amorphem und nanokristallenem Silizum	PhD Thesis	1965 wurde amorphes Silizium erstmals in einem Plasmaprozeß abgeschieden (ref. Sterling and Swann). Durch die Zersetzung von Silan (SiH4) ist im Plasma ein ausreichendes Angebot an Wasserstoff vorhanden, so daß ein Großteil der in der amorphen Structur offen gebliebenen Bindungen abgesättigt warden kann.

1999 JULY	SIMKOVIC V Virginia Polytechnic Institute and State University, Blacksburg, Virginia USA	Novel Low Dielectric Constant Thin Film Materials by Chemical Vapor deposition	MSc Thesis	Another technique of significance is plasma enhanced CVD (PECVD), which uses plasma instead of thermal activation to impart the necessary energy for the reaction to occur and was first reported in 1965 by Sterling and Swann for the deposition of amorphous silicon, SiO2 and Si3N4.
1999	Van der Vourt M Universiteit Utrect Holland	Dynamics of Vibrations in Amorphous Silicon	Proefschrift ISBN 90-393-2257-0	In the late 1960s it was discovered that thin amorphous silicon films can be grown by glow discharge deposition of silane (Ref. Sterling and Swann)
1999	JINGSONG YU etal State Key Laboratory of Silicon Materials Science Zhejiang University, Hangzhou China	Silicon Nitride Films Preparation	China Ceramic Industry 1999 No. 6 Volume 1 No.1	Since Swann and Sterling reported silicon nitride films suitable for passivation of silicon integrated circuits, silicon nitride films not only in the field of optoelectronic applications become widespread, and surface modification of materials in the field also have broad application prospects
1998 NOV	Young C.H, Korea Institute of Science and Technology Seoul South Korea	Semiconductor Process Plasma	Physics and High Technology Nov. 1998 No. 7 No. 9	Before plasma etching using the PECVD process of semiconductor-metal wiring shields, that can be deposited at low temperature SiN and SiO2 as a new generation was introduced ref. Sterling and Swann. After TI in 1975, came AMTs (Applied Materials) commercial PECVD equipment established itself in the 1980s as the essential semiconductor process equipment.
1995 JUNE	Trijssenaar M. Faculty of Electronic Components, Delft University of Technology, Delft, Holland	Hydrogenated Amorphous Silicon and p/i-hetero-junctions – Optical and Electrical Modeling as Applied to Solar Cells	PhD Thesis	In 1995, Sterling and Swann first reported the deposition of undoped a-Si:H produced by the Radio Frequency Chemical Deposition (RFCVD) of silane. The technique they used is essentially the same as that used today: silane gas molecules are disaociated by a radio frequency (r.f) plasma and the radicals formed deposit on a heated substrate.

1995	Badih El-Kareh (Approved by IBM)	Fundamentals of Semiconductor Processing Technology. Chapter 3.2 Chemical-Physical Deposition process Plasma P.102	Kluwer Academic Publishers USA ISBN 0-7923-9534-4 4th Printing 2002	PECVD oxide films are typically formed by the reaction of silane (or its halides) at ~350 deg. C. with O2, N2O or CO2 in a glow discharge. A silane and nitrous oxide gas mixture tends to produce oxide films with better uniformity than an oxygen reactant gas (references incl'g Sterling and Swann)
1995	Vogt K.W. Etal Georgia Institute of Technology, School of Chemical Eng. Atlanta, Georgia USA	Improvement in Dielectric Properties of Low Temperature PECVD Silicon Dioxide by reaction with Hydrazine	Journal of Electronic Material Vol. 24 No. 6 1995	Si-N absorptions at 833 cm-1 Ref. Sterling and Swann were not found. Within the sensitivity of FTIR, the PECVD films were composed of SiO2, silanol and water. No silicon nitride was identified.
1994	Chang C Y Francis Kai	GaAs High Speed Devices: Physics, Technology and Circuit Applications	Book by John Wiley and Sons ISBN 0-471-85641-X	Page 152 Ref. Fig. 4.29 Typical Data showing the Dielectric Constant of PECVD Silicon Nitride' Ref: Swann, Mehta and Cauge
1993 JULY	Hall G W Loughborough, University, Leicestershire UK	Control of the Properties of Semiconducting Thin Films Deposited using Magnetron Sputtering	PhD Thesis 1st July 1993	Amorphous silicon voltaics are almost exclusively thin film and hold the greatest promise for inexpensive cells at present. Following research into a-Si photo voltaics begun (32) Ref. Sterling and Swann in the late 1960's, the first devices were produced in 1974 (33) US Patent 4,065,521 Carlson, by the glow discharge decomposition of silane. The films contained hydrogen as a result of the decomposition, which acts to saturate dangling bonds at the micro voids and at other defects in the silicon film.

1993	Chanana R.K. Dwivedi R. Srivastava S. K Institute of Technology Banaras Hindu University Varanasi - 221 India	Effect of Annealing and Plasma Pre-cleaning on the Electrical Properties of N2O/SiH4 PECVD oxide as gate material in MOSFET and CCD.	Jnl. Solid State Electronics Vol, 36, No 7 pp 1021 -1026. Pergammon Press Ltd.	PECVD SiO2 films can be formed by reacting precursor gases like silane (SiH4), or silane derivations with an oxidant like CO2, O2, N2O etc in an RF or Microwave discharge. This dates back 27 years (Ref. Sterling and Swann Ref. 8 - 20)
1992	Brodie I Muray J	The Physics of Micro/Nano Fabrication	Book by Plenum Press New York ISBN 0-306-44146-2 1992	P.338 4.33 Plasma Enhanced Chemical Vapor Deposition (PECVD) Forming a plasma in the gas mixture both heats up the reagent molecules and forms more highly reactive radicals or ionised radicals (See section 3.6) This results in much lower substrate temperatures for the deposition process to take place. Table 4.4 Inorganic Films made by PECVD Silicon Oxide SiH4+N2O Sterling and Swan Silicon Nitride SiH4+NH3 Sterling and Swann Amorphous Si SiH4 Sterling and Swann Silicon Carbide SiH4+ C2H4 (or CH4) Sterling and Swann
1991 JUNE	Rosler R.S. Applied Materials Inc. Tempe, Arizona, USA	The Evolution of Commerceal Plasma Enhanced CVD Systems (Chemical Vapor Deposition)	Jnl. Of Solid State Technology June 1st 1991	An early example of the use of the low temperature capability of PECVD may be seen in the work of Swann in the late 1960s.. He found that PECVD silicon nitride deposited at 300 degrees C. using SiH4 and NH3 had electrical and barrier properties that made it suitable as a passivation film. Because its barrier properties (to Sodium and water vapor) are far superior to those of low temperature CVD oxides (undoped and phosphorus doped) plasma nitride provided a significant advantage for device stability, particularly when used with plastic encapsulated packages. A commercially available plasma deposition system, initially named Plasma 1 was introduced by Applied Materials in 1976.

1991 APRIL	Gupta M. Rathi V.K. Et al Semiconductor Eng. Lab. Dept. of Physics Indian Institute of Technology, New Delhi, India	The Preparation, Properties and Applications of Silicon Nitride Thin FilmsDeposited by Plasma Enhanced Chemical Vapor Deposition	Thin Solid Films. 204 (1991) PP 71-106	(1) The IR absorption characteristics of nitride film on silicon wafer measured between 500 and 25 deg.C are nearly the same in shape but the main absorption peak is shifted towards lower frequencies (from 870 to 820 cm-1)with decreasing temperature 9Ref. 69). This seems to be due to a structural loosening of the film as the temperature decreases (91) Ref. Sterling and Swann
1991	Han I.K. etal Korea Institute of Science and Technology, Cheongryang, PO box 131 Seoul Korea	Heating Effect I Plasma-Enhanced Chemical Vapour Deposion of Silicon Nitride	Journal of Material Science Letters Vol 10, Number 9 (1991) 526-528	Since Sterling and Swann first reported in 1965, the growth of silicon nitride films utilizing plasma enhanced chemical deposition (PECVD) for passivation of silicon devices, PECVD grown silicon nitride films have been extensively studied and used in microelectronics circuits manufacture.
1991	Miller L S Mullin J B General Editors of ' Materials: Silicon to Organics' Plenum Press , New York, USA	Chapter 11 'Amorphous Silicon-Electronics into the Twenty-First Century' by LeComber, P G	Book by Plenum Press, New York ISBN 0-306-43 655-8	3.0 Doping of a-Silicon To understand how this is done it is necessary to discuss how a-Si Films are prepared. The technique, originally developed in the Laboratories of STL in Harlow, Essex (2) (Ref. Sterling and Swann) is shown schematically in Fig. 3 Silane gas, SiH4, flows via a flowmeter F into a reactor over a substrate S which is heated to around 300 deg.C. The pressure inside the reactor is maintained at about 0.1 torr by vacuum pumps Using a few watts of power from a radio frequency generator, a weak glow discharge is excited between the two electrodes E1 and E2, one of which contains the heated substrate S. In this discharge the silane breaks down and a reddish brown a-Si film is deposited onto the substrate to a thickness typically of the order of 1um.
1991	P. de Neufville J., Izu M. Ovshinski S.R. Voltaix Inc. Branchburg, New Jersey, USA	Progress in Large Area Photovoltaic Devices based on Amorphous Silicon Alloys	Institute for Amorphous Studies Series 1991 pp214 - 217	It was Carlson's early collaboration with C. Wronski which served to rekindle scientific and technological interest in a-Si:H produced by the glow discharge induced decomposition of SiH4 gas and the decomposition of Si rich fragments of this gas onto substrates held at 200 - 300 deg.C. (Ref. Carlson and Wronski - Applied Physics Letters (28) 1976 p.671 and Sterling and Swann 1965.

1990 FEB	Smith D.L. etal Xerox Palo Alto Research Center, Palo Alto, California USA	Mechanism of SiNxHy Deposition from NH3-SiH4 Plasma	Jnl. Electrochem. Soc. Vol. 137, No. 2 1990	Here, we report on the ammonia-silane reactant mixture which was the first (Sterling and Swann) and still is the most widely used mixture.
1990 JAN	DeJoseph, Jr C. A. University of Oklahoma, Norman, Oklahoma and Wright Patterson Air Force Base, Ohio USA	Reactions of Silane in Active Nitrogen	PhD Thesis and Aero Propulsion and Power Lab. Report AD-A220 371	For the production of silicon nitride films, the silane is mixed with either nitrogen or ammonia, ref. Sterling and Swann. Silane is a gas which has important application in the manufacture of hydrogenated amorphous silicon (a-Si:H) for solar cells, xerographic photo receptors and other imaging detectors. It is also used extensively in the production of thin films of silicon nitride and silicon oxide in the fabrication of microelectronic devices. One of the most widely used methods for the production of these films is that of Plasma Enhanced Chemical Vapor Deposition (PECVD).
1989 JUNE	Kumar K.R. Dept. of Physics, Cochin University of Science and Technology, Cochin, India	Electrical Conduction and Dielectric Behaviour of Thin Films of Vacuum Evaporated Amorphous Silicon, Hydrogenated Amorphous Silicon and Chemically Deposited Cadmium Sulphide.	PhD Thesis Presented 20th June 1989	It was Sterling and Swann [28] at the STL laboratories who first prepared thin films of amorphous silicon and germanium by the decomposition of the hydride in an r.f. glow discharge in the mid sixties. R.F. plasma can be used to promote a reaction for example, between silane and NH3 to form durable and insulating films [28] Ref. Sterling and Swann.

1989 MAY	Vepzek S. Technical University Munich Germany	Fundamentals of the Plasma Induced and Assisted CVD: Plasma Parameters controlling the Chemical Equilibrium, The Deposition Kinetics and the Properties of the Films	Proceedings of The 7th European Conference on Chemical Vapour Deposition and Published in Journal de Physics Colloques Vol 50 No C5 May 1989	There is no reason to use plasma in the SiH4/O2 system. However, even the the thermal CVD applied to this system will produce SiO2, of poor quality, and hardly of any use, unless the deposition will be performed at high temperature in a diluted gas. If silicon dioxide of good electronic quality has to be deposited at a low temperature <350 degC., plasma induced CVD in the SiH4/NO-system is preferred. NO does not react spontaneously with silane and, therefore, the reaction can be induced as well as controlled by the discharge [36] Ref. Sterling and Swann.
!988 AUG	Roxlo C Exxon Research and Engineering New Jersey USA	Super Lattice Electro-optic Devices	Patent US 4,863,245 Filed 5th Sept 1989	Surface charge densities have been determined from capacitance-voltage characteristics in films deposited by rf glow discharge chemical vapour deposition, see e.g. Swann, Mehta and Cauge. 1969 and S.M. Hu ECS Jnl.
1988 JUNE	Spear W E Prof. Carnegie Laboratory of Physics, Dundee University, UK	Amorphous Semiconductors: a new generation of electronic materials	The Bakerian Lecture at The Royal Society HQ at Carlton House, London	Amorphous silicon (a-Si) deposited in a glow discharge plasma, an approach pioneered at the STL Laboratories in Harlow, (,Sterling and Swann 1965) proved to be an ideal model material and by the mid 1970s we had established the unique electronic properties of a-Si and also recognized the applied potential of this dopable and electronically controllable thin film material. World-wide industrial development of a-Si followed during the past 10 years and these add justification to the title of the talk.
1987 AUG	Shen Y Chang J Et al University of Science and Technology, Hefei, Anhui, China	Preparation and Gas Sensing Characterisation of Fe2O3 Thin Films by Plasma CVD	Paper Presented at ISPC-8, Int. Symp. on Plasma Chemistry , Tokyo Japan	Plasma enhanced CVD techniques have been widely used to prepare various films, silicon nitride(8) Ref Swann, Mehta Cauge and Amorphous silicon (10) Ref. Sterling and Swann US Patent3,655,438 (1971)

1984 DEC	Archibald J W University of Durham, UK	Electrical Characteristics of Amorphous Silicon Schottky Barriers	PhD Thesis	Chapter 3 Hydrogenated Amorphous Silicon 3.1 Introduction Hydrogenated amorphous silicon was first produced at the STL laboratories Ref 1 Sterling and Swann [1965], Ref. 2 Chittick, by the glow discharge decomposition of silane (SiH_4). The properties of these amorphous silicon films were very dependent on the glow discharge parameters, but it was nevertheless recognised that the films were always much more resistive than thermally evaporated amorphous silicon, as also it was found that the density of defects was much lower.
1984 OCT	Venugopalan M. Western Illinois University. Avni R. NASA Lewis Research Centre Cleveland, Ohio USA	Analysis of Glow Discharges For Understanding The Process Of Film Formation	NASA Technical Memorandum TM-83750	Sterling and Swann Swann, Mehta and Cauge Table 1X - Inorganic Films deposited by PCVD and full references on Pages 74 and 75.
1984 OCT	Roxlo C Persans D Exxon Research and Engineering New Jersey USA	Super Lattice Piezoelectric Devices	Patent US 4,590,399 May 20th 1986	Surface charge densities have been determined from capacitance - voltage characteristics on films deposited by rf glow discharge chemical vapour deposition, see for example Swann, Mehta, Cauge Jnl Electrochemistry Soc. 1969
1984 APRIL	Flasck R. Holmberg S. Alphasil Inc. Fremont, California, USA	Active Matrix Liquid Crystal Displays using Amorphous Silicon thin film transistors.	IEEE Computer Graphics and Applications Issue No. 04 pp 19 - 22	The major challenge facing the portable computer industry is the development of cost effective, low power, full screen, flat panel displays. Here is the technology that can help. Ref. 1 Sterling and Swann.
1984	Gorczyca T B Gorowitz B General Electric Corp. R&D Schenectady New York, USA	Plasma-Enhanced Chemical Vapor Deposition of Dielectrics. Chapter 4	Modern Materials: Advances in Development and Applications Edited by: Einspruch N Brown D M Academic Press Inc.Orlando Fla . Library of Congress, Cat, Card No. 58-12811	Chapter 4 111. Specific Materials A. PECVD Silicon Nitride The deposition of silicon nitride in a high frequency glow discharge was first described by Sterling and Swann in 1965 [17]. The reactants typically used are silane and ammonia. B. PECVD Silicon Dioxide Sterling and Swann reported the glow discharge deposition of silicon dioxide in 1965 [17]. The reactants typically used are silane and nitrous oxide and/or oxygen.

1979 MAY	Chu T L Westinghouse Research Laboratories, Pittsburgh, Pennsylvania, USA	Chemical Deposition of Dielectrics for Thin Film Circuits and Components	SCP and Solid State Technolo gy Pp 36 to 41 ref. 33	Recently, the deposition of amorphous silicon nitride films on silicon substrates has been accomplished by the reaction of silane and ammonia at high temperatures or by using an r.f. discharge technique (Ref. Sterling and Swann) at 300 degC having similar properties
1979 APRIL	Penn, Thomas Clifton Texas Instruments Research Laboratory, Dallas,Texas USA	Forecast of VLSI Processing – A Historical Review of the First Dry-Processed IC	IEEE Transacti ons on Electron Devices Vol. ED-26, No.4, April 1979	Historically our interest in plasma processing arose from the deposition of silicon nitride by Sterling and Swann
1979 JAN	Kocia P. Mayor G. et al Laboratory of Applied Physics, Fed. Institut of Technology, Lausanne, Switzerland	Some Properties of the Low Pressure Discharge in Silane	Jnl. de Physique Colloques Submitted 1st Jan 1979	During past several years, there has been a growing interest in the silane (SiH_4) as a material for the introduction of silicon and its film (1,2)-Sterling and Swann. There are several methods to produce the films of Si. The deposition in a glow discharge in silane seems to have some advantage regarding the other methods like evaporation in vacuum or cathodic sputtering.
1976 JUNE	Rosler S Benzing W C Baldo J Applied Materials Inc. Santa Clara Calif. USA	A Production Reactor for Low Temperature Plasma-Enhanced Silicon Nitride Deposition	Solid State Technolo gy June 1976	In 1967, Swann, et al, reported that…".(Plasma promoted) low temperature nitride is suitable for passivating silicon planar devices," the very topic that is creating all the interest today

1974 SEPT	Campbell D S University of Technology Loughborough, Leicestershire, UK	Preparation Methods for Thin Films	Physics of Non-Metallic Thin Films Plenum Press London 1976 ISBN-13 978-1-4684-0849-2 Presented in Corsica,Serra di Ferro Sept.1-5 1974	Glow Discharge conditions can also be used to effect vapor phase reactions such as the deposition of silicon nitride from a gaseous mixture of silicon hydride, ammonia and hydrogen (38) Ref. Sterling and Swann
1970 NOV	Foster J.E. Swartz J.M. The National Cash Register Company and Ohio State University Colombus Ohio Respectively USA	Electrical Characteristics of the Silicon Nitride-Gallium Arsenide Interface	Jnl. of The Electrochem. Society. Vol. 117 No 11	There has recently been a great deal of attention (3-35) including Ref 16 Sterling and Swann and Ref 29 Swann, Mehta and Cauge focussed on amorphous silicon nitride (Si3N4) as a passivating and masking film partly or fully replacing silicon dioxide. Silicon Nitride is much more impervious to diffusants of all kinds than silicon dioxide. In addition, the use of silicon nitride as an insulator in a metal-nitride-semiconductor (MNS) FET increases the transconductance and drain current compared to SiO2 by 50% because of its higher dielectric constant.
1970	Locker L D Bell Tel Labs. Murray Hill New Jersey USA	Materials Produced by Electrical Discharge	Modern Materials: Advances in Development and Applications Academic Press Inc. New York Bruce W. Goner Library of Congress Catalog. Card No. 58-12811	Page 110 The glow discharge reaction between silane and ammonia can be brought about even with a refrigerated substrate, but more desirable properties are obtained between 250-300 deg.C. Sterling and Swann (43) found that silicon nitride films formed on a cold substrate are etched more rapidly in hydrofluoric acid than when the substrate temperature is 300 deg.C. Page 118 a. Silicon Dioxide The primary advantage of the glow discharge technique is that the oxide is formed at a relatively low temperature. Heating of semiconductor devices can cause irreversible changes in their properties due to redistribution of impurities. For example, the current voltage characteristics of metal-insulator-semiconductor transistors is changed considerably by the diffusion of sodium during thermal treatment (36) Ref. Swann, Mehta and Cauge.

1969 DEC	Aboaf J.A. IBM Watson Research Ctr. Yorktown Heights, N.Y. USA	Some Properties of Vapor Deposited Silicon Nitride Films obtained by the reaction of SiBr4 and NH3	Jnl. of The Electrochem. Society Vol. 116 No 12	Silicon Nitride films are prepared by various methods: reaction between silane and ammonia at temperature above 750 deg.C (1 - 3), and at low temperature by a radio frequency glow discharge reaction (4) - Ref Swann, Mehta and Cauge or by sputtering (5). These methods lead to silicon nitride films of Si3N4 composition: they are resistant to moisture and are a good mask against shallow diffusion.
1969 AUG	Feist W.M. Steele S.R. Readey D.W. Research Div. Raytheon Company, Waltham, Mass USA	The preparation of Films by Chemical Vapor Deposition	Physics of Thin Films. Advances in Research and Develop't. Vol. 5 by G..Hass R.Thun Academic Press Inc. New York	Page 292 Sterling and Swann (Ref 233) produced films of SiO2, Si3N4 and Si by supplying the energy necessary to sustain the deposition reaction of the mixed gaseous reagents through an rf discharge etc. etc. Page 298 Swann et al (Ref 247) deposited Si3N4 from SiH4 and NH3 fed into the system, with flow ratios ranging from 0.03 to 0.5, on substrates held at temperatures of 300 to 550 deg.C. The deposition rate increased nearly linearly with the SiH4:NH3 ratio (from <40 to 180 Ang/min at 300 degC however, etc. etc.
1969 JULY	Swann R.C.G. Pyne A.E. ITT Semiconductors, Research Lab., West Palm Beach, Fla. USA	The Preparation and Properties of Silica Films Deposited from Silane and Carbon Dioxide	Jnl. of The Elctrochem. Society Vol 116 No 7	Many silicon dioxide deposition systems have been investigated, for example, the direct oxidation of silane (1), decomposition ethyl-triethoxy-silane (2), the reaction of silicon halides with carbon dioxide (3-5) as well as sputtering (6+7) and glow discharge reaction (8) Ref Sterling and Swann. The effect of free silicon on the dielectric loss in silicon nitride has previously been reported (13) Ref Swann, Mehta and Cauge.
1969 JUNE	Secrist D.R. Mackenzie J.D IBM Corp. Poughkeepsie New York and Rensselaer Polytechnic, Troy,New York USA	Vapor Phase Formation of Non-Crystalline films by a microwave Discharge Technique	Advances in Chemistry Vol. 80 American Chemical Society ISBN 13: 9780814	Sterling and Swann [7] have recently deposited amorphous Si3N4 films by the reaction of silane and anhydrous ammonia in an RF discharge

1969 APRIL	Drake C F Alexander J F STL Harlow Essex UK	Glassy bistable electrical switching and memory device	US Patent 3440588 A Int. Standard Electric Corp.	Yet another method of making a device is to pass a glow discharge through a low pressure mixture of oxygen and volatile compounds of the elements from which the glass is made with a heated metal substrate suitably placed to receive a deposit of the glass. The latter process can be conducted according to the teaching of US Patent Application No. 452,487 Sterling and Swann
1969 FEB	Chittick R.C. Alexander J.H Sterling H.F. STL Harlow England	The Preparation and Properties of Amorphous Silicon	Jnl. of The Electrochem. Society Vol. 116 No 1	If silane gas at low pressure is subject to a high frequency electrode-less glow discharge, the deposition of amorphous or vitreous silicon takes place (1) Ref. Sterling and Swann. Although higher electron temperatures exist in the gas it is molecularly near room temperature, so that deposition on to a virtually cold substrate results in very short range ordering in the structure which is not necessarily of tetrahedral form.
1969	Buck T M National Research Council Washington DC USA	Surface Noise in Semiconductor Detectors	Proceedings of a Conference on Instruments and Techniques, Nuclear Science National Academy of Sciences Washington DC Pub. 1593	Basic Detector Processes. Ref. Table 1 Insulator Film Processes - Page 148. Ref.14. Sterling and Swann Silicon Dioxide rf glow discharge 30-900 degC. Silicon Nitride rf glow discharge30-900 degC. Oxide passivation of silicon devices was in its infancy in the early days of semiconductor detector technology. Its use on detectors was discovered by Gibson ref. 14
1968 SEPT	Brown G.A. Robinette WJr Carlson H.G. Texas Instruments Dallas Tx. USA	Electrical Characteristics of Silicon Nitride Films Prepared by Silane-Ammpnia Reaction	Jnl. Electrochem. Society Vol. 115 No 6	The Preparation of SiliconNitride in thin films by the reaction of silane and ammonia in hydrogen diluent has been reported by several workers (1-4) and is one of several techniques by which films of the material have been formed (5) Ref. Sterling and Swann.
1968 MAY	Grieco M.J. Worthing F.L. Schwartz B. Bell Tel.Labs Murray Hill New Jersey USA	Silicon Nitride Thin Films from SiCl4 plus NH3: Preparation and Properties	Jnl. of The Electrochem Society Vol. 115 No 5	A number of investigators (12) - Sterling and Swann and (1) Hu S.M. have made use of various high field discharge techniques in order to obtain nitride deposition at low temperatures.

1968 MAR	Deal B.E. Fleming B.J. Castro P.l. Fairchild Semiconductor. Research and Dev. Labs, Palo Alto. California USA	Electrical Properties of Vapor Deposited Silicon Nitride and Silicon Oxide Films on Silicon	Jnl. of The Electrochem. Society Vol. 115 No 3	In 1965, Sterling and Swann reported a method for depositing films involving chemical reactions in an r.f, discharge. These films included silicon, silicon dioxide and silicon nitride.
1968 FEB	Saxena A.N. Tkal O. Sprague Electric Comp North Adams Research and Dev. Labs. Massachuset's USA	Determination of the Etch Rate and the Refractive Index of Silicon Nitride Films with an Ellipsometer.	Jnl. of The Electrochem Society Vol. 115 No 2	In the first method the silicon nitride film, 5300 Ang. thick was deposited on 10 Ohm.cm (111), p-type Si using reactive sputtering in N2. In the second method (2) Ref. Sterling and Swann and Swann, Mehta and Cauge, the silicon nitride film, 4000 Ang. thick, was deposited on 10 Ohm-cm (111), p-type silicon using chemical vapour deposition (NH3 + SiH4) in a glow discharge at 400 Deg.C
1967 NOV	Levitt R.S. Zwicker W.K. Philips Laboratories Briarcliff Manor New York USA	Infrared Spectrum of Si3N4 on GaAs	Jnl. of Electrochem. Society Vol. 114 no 11	The characteristic infrared absorption of Si3N4 occurs in the 8-14 micron wavelength region (2) Ref Sterling and Swann.
1967 SEPT	Yoshioka S. Takayanagi S. Research Labs Matsushita Electronic Corporation Takasaki Osaka Japan	Deposition of Silicon Nitride by the Silane-Hydrozine Process	Jnl. of the Electrochem. Society Vol. 114 No 9	Formation of Silicon Nitride films have been reported by reaction of silane and ammonia under a r.f. discharge (1) Ref Sterling and Swann

1967 JULY	Chu T.L. Lee C.H. Gruber G.A. Westinghouse Research Labs Pittsburgh Pennsylvania USA	The Preparation and Propertiies of Amorphous Silicon Nitride Films	Jnl. of The Electrochem. Society Vol 114 No 7	The reaction between silane and ammonia is less complex involving presumably the formation of silicon-hydrogen radicals or silicon and its subsequent reaction with ammonia. The deposition of amorphous silicon nitride films has been accomplished by this reaction using an rf discharge technique (11) Ref. Sterling and Swann
1967 JULY	Hu S.M. Gregor L.V. IBM Components Div. East Fishkill N.Y. USA	Silicon Nitride Films by Reactive Sputtering	Jnl. of The Electrochem. Society Vol. 114 No 8	Sterling and Swann (3) and Doo et al (4)have succeeded in the deposition of continuous amorphous silicon nitride films by means of vapour phase reaction of silane and anhydrous ammonia
1967 JULY	Bean K.E. Gleim P.S. Yeakley R.L Texas Instruments Dallas Tx. and Runyan W.R. S. M. University, Dallas USA	Properties of Vapor Deposited Silicon Nitride Films using the SiH4/NH3/H2 System	Jnl. of The Electrochem.Society Vol. 114 No 7	Several methods for the synthesis of Silicon Nitride have been reported (1-8) Ref. including Sterling and Swann
1967	Doty C T 3M Corp. St. Paul Minnesota USA	Digest of Literature on Dielectrics Vol. 31 1967	Prepared by Division of Engineering. National Research Council National Academy of Sciences Pub. 1595 Washington DC Library of Congress Card No 45-33864	Page 110 Failure of Thin Films - Dielectric Breakdown of Solids Swann and co-workers (67) deposited Si nitride by reacting silane and NH3 in a radio frequency glow discharge. Physical and electrical properties, including breakdown strength, were correlated to changes in concentration of these components in the gas.

1966 DEC	Doo V Y Nichols D R Silvey G A IBM Components Div. East Fishkill N. Y. USA	Preparation and Properties of Pyrolytic Silicon Nitride	Jnl. of The Electrochem. Society Vol. 113 No. 12	Sterling and Swann reported that silicon nitride film has been obtained by the reaction of of silane and ammonia at a pressure of around 0.1 torr under rf discharge. Also,the IR absorption peak of the silicon nitride films prepared by r.f. discharge is very broad, from 10 – 14 microns with a maximum at 12 microns.. The films prepared by the pyrolytic process shows a peak from 10 - 12 microns
1966 JULY	Hu S.M. IBM System Dev. Div. East Fishkill N.Y. USA	Properties of Amorphous Silicon Nitride Films	Jnl. of The Electrochem. Society Vol. 113 No 7	It appears that the first published successful attempt to prepare films of silicon nitride is the recent work of Sterling and Swann
1966 JULY	Gregor L.V. IBM System Dev. Div. East Fishkill N.Y. USA	Chapter 4.0 Glow Discharge	Physics of Thin Films. Advances in Research and Develop'tt. Vol. 3 by G..Hass Academic Press Inc. New York	Page 138 A glow discharge in mixtures of SiH4, NH3 and H2 has been used to deposit amorphous films said to be Si3N4 (Ref) Sterling and Swann

APPENDIX B

- List of Patents.

Patents Granted:

French Patent.1442502: Sterling and Swann, Filed 5 August 1964,Published 17 June 1966
Perfectionnements aux methods de formation de couches

British Patent 1,104,935: Sterling and Swann. Filed 7 May 1965, Published 6 March 1968
Improvements in or relating to a method of forming a layer of an inorganic compound.

British Patent 1,136218: Sterling, Dobson, Swann and Selway. Published 11 Dec 1968
Improvements in or relating to the manufacture of semiconductor Optical Devices.

US Patent. 3,485,666: Sterling and Swann. Filed 3 May 1965, Publish 23 Dec. 1969.
Method of forming a silicon nitride coating.

US Patent. 3,576,684: Mehta and Swann. Filed 12 August 1968, Publish 27 April 1971
Aluminium-alloy junction devices using silicon nitride as a mask.

US Patent. 3,576,685: Swann and Cauge. Filed 15 March 1968, Publish 27 April 1971
Doping semiconductors with elemental dopant impurity.

CA Patent. 847296: Sterling and Swann. Issued 23 July 1970
Methods of layer formation

US Patent. 3,649,888: Pitzer, Braddock, Swann and Pyne. Filed 14 May 1969
Published 14 March 1971
Dielectric structure for semiconductor device

DE Patent. 1932372A. Mehta, Cauge and Swann. Filed 26 June 1969
Published 26 Feb 1970
Siliziumnitridemaskierung bei der herstelling von mit Aluminium legierten sperrschichtbauelementen.

US Patent. 3,655,438: Sterling and Swann. Filed 20 Oct. 1969. Filed 11April 1972
Method of forming silicon oxide coatings in an electric discharge

US Patent. 3,749,610: Swann and Penton. Filed 11 Jan. 1971. Filed 31 July 1973
Production of silicon insulated gate and ion implanted field Transistor.

DE Patent. 2133295A. Swann, Penton, Pyne. Filed 7 May 1971. Published 13 Jan '72
N-Kanal Siliziumgitter Transistor des Anreicherungs Type.

US Patent. 3,761,327: Harlow, Swann, Penton and Bakker. Filed 19 March 1971
Published 25 September 1973
Planar silicon gate MOS Process

Significance of these Patents:

The significance and/or importance of a patent may be assessed by the number of subsequent patents produced by other Companies which, in turn, refer to the original patent.
This particular study was made around 2010 and not updated but is included to aid any other researchers.

This listing below excludes the two British Patents and one Canadian Patent which are not as accessible as the US Patents. The US patents are listed below in order of their decreasing number of referenced patents and their time span of generation, from the first patent filed to the most recent issued, as follows:

			# of Ref.	Referenced Patents.	
Patent	Issue	Filing.	Patents.	First Filing Date.	Last Issue Date.
US 3485666	03/05/65	(23/12/69).	65	25/08/75.	28/11/06
US 3655438.	20/10/69	(1972).	42	13/07/78.	20/04/10
US 3576685	15/03/68	(27/04/71).	37.	10/01/75.	21/12/10
US 3761327.	19/03/71.	(25/09/73).	16.	22/04/75.	31/07/84
US 3749610.	11/01/71.	(31/07/73).	7.	14/04/76.	13/11/01
US 3576684.	12/08/68	(27/04/71.	3.	14/07/76.	18/12/90
US 3649888.	14/05/69.	(1972).	1.	27/09/90.	14/01/92

The Companies referencing these Patents are as follows:

US 3485666

IBM (x4), RCA (x4), MONSANTO (x1), SONY (x1), BELL LABS (x2), TOKYO SHIBAURA (TOSHIBA) (x4), GENERAL INSTRUMENTS (x1), US GOVERNMENT- ARMY (x1), WESTERN ELECTRIC (x1), SIEMENS (x1), HP (x1), INT. STD. ELECTRIC (x1), MBB (x1), NATIONAL RES. DEV. (x1), VLSI TECH'y RES. ASS'N (x1), Dir. Gen. Science and TECH'y Japan (x1), MIT (x1), HITACHI (x1), ROBERT BOSCH (x1), THOMSON CSF (x1)
The above Patent is listed on the Smithsonian Institute Web site under National Museum of American History

US 3655438

AIRCO INC. (x1), LFE CORP. (x1), PHILIPS US (x1), RCA (x2), PLASMA PHYSICS CORP (x2), USA (AIR FORCE) (x1), NORTHERN TELECOM (x1), UNIVERSITY OF CALIFORNIA (x1), INT. STD. ELECTRIC (x1), IBM (x1), FUJITSU LTD. (x1), CANADIAN IND. INNOVATION (x1), CANON (x6), ENERGY CONV. DEV. (x1), AT&T LABS (x2), USA

(ARMY) (x1), LUCENT TECH'Y (x1), LAM RESEARCH (x2), SEMI. EQUIP. INC. (x1), SAMSUNG ELECTRONICS (x3), MURAKAMI CORP. (x1), OMNIGUIDE INC. (x3), CREE INC. (x1)

US 3576685

USA - Dept. ENERGY (x1), MITSUBISHI - DKK (x1), FUJI ELECTRIC CORP. (x1), XEROX CORP. (x1), KK TOSHIBA (x1), SEIKO INSTRUMENTS (x1), APPLIED MATERIALS INC. (x31)

US 3761327

RCA (x2), IBM (x3), PHILIPS - US (x2), INTEL (x2), TOKO INC (x1), NIPPON ELECTRIC (x2), BELL LABS (x2).

US 3749610

HITACHI LTD (x1), RCA CORP (x1), SAMSUNG ELECTRONICS (x2), NATIONAL SEMICONDUCTOR (x2), ADVANCED MICRO DEVICES (AMD). (x1)

US 3576684

SOLAREX (x1), HARRIS CORP. (x1), MOTOROLA (x1)

US 3649888

HITACHI LTD (x1), RCA (1), SAMSUNG ELECTRONICS (x2), NATIONAL SEMI. (x2), ADVANCED MICRO DEVICES (AMD). (x1)

The companies referencing most of the above Patents are listed in order below:

APPLIED MATERIALS = 31, RCA = 10, IBM = 8, SAMSUNG ELECTRONICS = 7, AT&T (ATT LABS, BELL LABS, WESTERN ELECTRIC) =7, CANON =6, TOKYO SHIBAURA (TOSHIBA)= 4, NATIONAL SEMICONDUCTOR = 4, PHILIPS US = 3, OMNIGUIDE = 3

APPENDIX C

- **Publications:**

"Growth of Silicon Layers by Thermal Decomposition of 'Silane"
by DJD Thomas and R C G Swann. July 1962
'STL Internal Report No. 366'

"Gas etching and selective deposition of silicon"
by HF Sterling, RCG Swann and MPC Patel.
' STL Internal Report No. 130 1964' Released 27 January 1965', 13 Pages.

"The Preparation and Properties of Silicon Dioxide Layers" using Glow Discharge
by R C G Swann and (Part Time: H F Sterling and D J D Thomas)
STL Internal Report RP7-30 1965.

"Vapour Phase Deposition promoted by Radio Frequency Discharge"
by H F Sterling and R C G Swann.
'STL Internal Report No. 477'

"Chemical Vapour Deposition promoted by rf discharge"
by HF Sterling and RCG Swann.
'Solid State Electronics' vol.8 653 - 654 March 1965
154 Citations

"Vapour deposition of inorganic coatings in a glow discharge"
by HF Sterling and RCG Swann
'Proceedings - New Materials and Processes in Instrument Manufacture' at SIRA Conference, Eastbourne 13 - 14 May 1965

"The radio frequency initiated vapour deposition of glassy layers"
by HF Sterling and RCG Swann.
'Physics and Chemistry of Glasses' vol. 6 No 3 Pp. 108-110 June 1965.
Cited in Patent:US 3503798 Filed by Matsushita electronics Corp. Oct. 23 1967

"The Preparation and Properties of Thin Film Silicon - Nitrogen Compounds Produced by a Radio Frequency Glow Discharge Reaction" by RCG Swann, RR Mehta and TP Cauge,
J. Electrochem. Soc. Vol. 114 No. 7 July 1967 pp 713 - 7170
61 Citations

"The Preparation and Properties of Silica Films Deposited from Silane and Carbon Dioxide" by RCG Swann and AE Pyne
J. Electrochem. Soc. Vol. 116 No. 7 July 1969 pp 1014 - 1017
6 Citations

"Hot Carrier Degradation in sub-micron CMOS technologies ~ A comparative study".
By J. Vandenbroeck, H. Rempp and R. C. G. Swann.
Proceedings of the Third International Symposium of Electronic Materials and Devices.
The Electrochemical Society 1994 pp 277 - 285.

Lieferanten-Audit ALS Element der vorbeugenden Qualitätssicherung by R C G Swann. Published in QZ Qualitat und Zuverlassigkeit in November 1991 36.Jg, 11/1991,5.238-253. Organ der Deutschen Gesellschaft fur Qualitat.

APPENDIX D

Presentations and Exhibits

November 1964. Slough College of Technology. Lectured in a series on 'Semiconductor Technology'.

February 23rd 1965. Atomic Weapons Research Establishment, Aldermaston. (L W Owen) Lectured on Thin Film Depositions by Pyrolysis (Silicon Tetrachloride and Silane) and by an r.f Discharge technique.

February 24th 1965. Imperial College, London University. Dept. of Chemical Engineering and Chemical Technology, Prince Consort Road, South Kensington. Lectured on 'Vapour Phase Deposition of Thin Films' to research groups in industry and the college.

April 5th - 8th 1965. Exhibited laboratory built equipment at The Physics Exhibition - Manchester College of Science and Technology sponsored by The Institute of Physics and The Physical Society.
"Glow discharge apparatus for the deposition of amorphous layers ~ silicon, silicon oxide, silicon nitride, etc".

May 13th - 14th 1965. SIRA (British Scientific Instrument Research Association) at The Grand Hotel, Eastbourne.
"Vapour Deposition of Inorganic Coatings in a Glow Discharge".
1965. Chelsea College, London (Institute of Physics). 'Glow Discharge Deposition of Materials'

June 1965. Sheffield University. Physics and Chemistry of Glasses Conference sponsored by the Society of Glass Technology.
"The Radio Frequency initiated vapour deposition of Glassy Layers"

October 1966. Fall Meeting of The Electrochemical Society Meeting in Philadelphia
"Properties of Silicon Nitride Deposited from a Gaseous Source by R.F. Glow Discharge"
By R.C.G Swann

May 8th - 12th 1967. Spring Meeting of The ElectroChemical Society at Dallas Hilton, Dallas, Texas.
"Anomalous Dielectric Behaviour of Silicon Nitride"
By R.C.G. Swann, R.R. Mehta and T.P. Cauge

May 8th - 12th 1967. Spring Meeting of The ElectroChemical Society at Dallas Hilton, Dallas, Texas
"Redistribution of Donor and Acceptor Impurities in Silicon during Deposition and Subsequent Reheat of Silicon Nitride"
By T.P. Cauge, R.R. Mehta and R.C.G. Swann

October 11th - 14th 1967. Fall Meeting of The Electro Chemical Society in Chicago, Illinois.
"Silicon Nitride Deposited at Room Temperature ~ Physical and Chemical Properties"
By R.C.G. Swann, R.R. Mehta, D.A. Bunzow and T.P. Cauge

October 11th - 14th 1967. Fall Meeting of The Electro Chemical Society in Chicago, Illinois.
"Improved MIS Transistor Performance using Oxide - Nitride Combinations as the Dielectric"
By T.P. Cauge, R.R. Mehta, R.C.G. Swann and W.M. Ford

May 1968. Spring Meeting of The Electro Chemical Society Meeting in Boston, Mass.
"The Pyrolytic Deposition and Properties from Silane and Carbon Dioxide
By R C G Swann.

May 1968. Spring Meeting of The Electro Chemical Society Meeting in Boston, Mass.
Recent News Item 305
By R C G Swann, A E Pyne and T P Cauge.

January 19th 1970. Lectured at The University of Florida, Gainsville, Florida, on
"The Theory and Practice of MOS Transistors" by R C G Swann, Research Manager,
ITT Semiconductor, West Palm Beach, Fla.

September 12th - 15th 1972. The Second European Solid State Devices Research Conference (ESSDERC) organised by The Institute of Physics, held at The University of Lancaster.
“Realisation of a N-Channel Silicon Gate 4X4 Crosspoint Integrated Circuit designed and produced at STL Harlow”, by T Rowe, R C G Swann and H Gamble.

October 4th - 7th 1994. The 5th Symposium on Reliability of Electron Devices, Failure Physics and Analysis, Glasgow, Scotland.
“Hot Carrier Degradation, in Submicron CMOS Technologies: A Comparative Study By J. Vandenbroeck, Alcatel Bell, Antwerp, Belgium, H. Rempp, Alcatel SEL, Stuttgart, Germany and R C G Swann, Alcatel, Zug, Switzerland.