High deposition rate a-Si:H layers from pure SiH_4 and from a 10% dilution of SiH_4 in H_2

M. Estrada, A. Cerdeira, and S. Soto
Depto. de Ingeniería Eléctrica -S.E.E.S., CINVESTAV
Av. Instituto Politécnico Nacional 2508, 07300 México D. F.

I. Pereyra
Laboratory of Microelectronics- University of Sao Paulo, Brazil

In this paper, we present results of the deposition rates and the characterization of a-Si:H layers deposited from pure SiH_4 in a 13.56 MHz Plasma Enhanced Chemical Vapor Deposition (PECVD) equipment, where the use of parallel plates of equal area, long gas residence as well as the optimization of process parameters permitted to double previously reported deposition rates obtained employing this rf frequency and gas. A deposition process using a 10% dilution of SiH_4 in H_2.was also optimized to increase the deposition rate to 1,5 µm/hr. I-V and I-T curves of PIN diodes up to 18 µm thick fabricated on these high deposition rates a-Si:H layers were characterized. The density of ionized states at deep depletion were determined and compare with those obtained for diodes fabricated with other standard and high deposition rate methods

1. Introduction.

During the last years, much effort has been dedicated to fabricate thick amorphous PIN diodes that can be used in applications such as radiation detectors for medical applications. PIN diodes several micrometers thick are already commercially available for the indirect detection of medical x-rays, used in conjunction with scintillate layers to transform the radiation into photons [1]. Direct detection is still an objective to achieve. Layers tens or hundreds micrometers thick, stable and with good electrical parameters are required, and so it is necessary to increase the deposition rate of the PECDV films, maintaining or improving their quality. To achieve this objective, several approaches have been used: increase the rf frequency, increase the plasma density or dilute the SiH_4 in other gases. By using a rf frequency of 85 MHz, good quality a-Si:H layers with deposition rates above 2 µm/hr have been obtained by PECVD using pure SiH_4 or mixtures of SiH_4 in He, and in H_2 [2]. At 13.56 MHz, a deposition rate of 2.88 µm/hr has been reported for a dilution of SiH_4 in He [3]. For pure SiH_4 the deposition rate is usually less than 1 µm/hr in a standard PECVD equipment [4]. In Ref. [5], a deposition rate of 11 µm/hr was reported using a modified reactor where the substrates were located in the electrode with the smallest area. However, these authors recognize that as deposited films had an inferior quality when compared to conventionally deposited material.

A deposition rate using a gas mixture of 10% SiH_4 in H_2 that provides deposition rates in the order of 0,9 µm /hr was already reported by us when a specially designed injector was used [6]. In Ref. [7] we reported a deposition rate of up to 2.5 µm/hr for pure SiH_4 using a plasma frequency of 13,56 MHz.

In this work we characterize films and diodes deposited in a standard PECVD equipment, at 13.56 MHz from pure SiH_4, (process PA1) and 10 % SiH_4 in H_2, (process PA2), when an injector and parallel plates of equal area are used.

2. Experimental details.

The process parameters that can increase the deposition rate in a PECVD equipment are the power density, the deposition temperature, the pressure and the flow rate, as well as the geometry of the reactor and gas flow mixture. Increasing power density may influence negatively the properties of the deposited layers, due to higher ion bombardment and/or gas phase polymerization, which can also occur when increasing the flow rate.

Increasing the deposition temperature may increase the gas reactivity and the rate of the surface reaction, but the concentration of hydrogen atoms inside the a-Si:H layers is also related to the temperature of deposition and a total concentration smaller than 20 % must be achieved to obtain good quality with low density of dangling bonds and film stress.

As described by Paschen's Law, for each individual geometry of the deposition equipment there are two regimes: the low pressure regime, where the deposition is limited by surface reaction, and the high pressure regime, where deposition is limited by chemical processes in the gaseous phase. In this later case, formation of Si-H bonding of higher levels (SiH_2, etc.) are more expected than in the first regime, where the predominant Si-H bonding is expected to be SiH. Both PA1 and PA2 processes were adjusted to work under the low pressure regime.

In our experiments the geometry of the reactors was modified to provide parallel electrodes of equal area. The use of electrodes of equal area results in a greater sheath

voltage for the electrode where the substrates are located, so the deposition rate is increased.

Process PA1 was first adjusted in two reactors schematically shown in Fig. 1 [6], and later in the reactor shown in Fig 2, which indicates that the reported process is repeatable.

The layer thickness was measured by profilometry and reflection spectrometry. The presence of Si-H bonds was determined by Fourier Transform Infrared Spectrometry (FTIR).

The flow rate can be increased specially when diluted SiH_4 is used, but it is limited by the extraction capacity of the vacuum equipment to maintain the condition of low pressure regime. The use of a gas injector that provides the gas to flow parallel to the surface of the substrate where the layer is being deposited was already reported to have great importance for obtaining high deposition rates using 10% dilution of SiH_4 in H_2 [6]. Under these conditions, we could enhance the concentration of the reactive species near the substrate surface, without increasing gas phase polymerization.

Cr deposited on silicon and glass substrates were used. Before deposition, the substrates were carefully cleaned in triclorethylene, acetone, a mixture of sulfuric acid and H_2O_2, a mixture of H_2O_2 with NH_4OH, and a mixture of H_2O_2 with ClH, followed by a rinse in deionized water. Cleaning of the substrate was of much importance to increase film quality and to avoid peel off.

PIN diodes were fabricated on silicon substrates previously covered with a Cr layer, to define the back electrode of the diodes. The n+ type amorphous layer 170 nm thick was deposited from a mixture of 10% SiH_4 in hydrogen and 1% PH_3 in H_2; p^+ layers 300 nm thick were deposited from a mixture of 10% SiH_4 in H_2, and 1% of B_2H_6 in H_2. For PA1 process, the i-layer was deposited using 20 sccm of pure SiH_4 at 43Pa, 50 mW/cm^2 and 200 ^{o}C; For all samples, the p^+ layer was covered by another layer of Cr, to form the contact region. Afterwards, a photolithography was made, on the Cr layer, the p^+ layer and part of the i-layer. In order to leave the metal and the p^+ layer only in the areas defined for the independent diodes. The etching of part of the i-layer around the diode area is done to prevent leakage current through the border of the p-i junction. Finally an annealing to form the ohmic contacts was done.

To characterize PIN radiation detectors, it is important to determine the voltage, V_{fd}, required to reach the condition of full depletion of the intrinsic layer. A space charge region (SCR) across this layer and an electric field to help recollect the generated carriers are both required for a good performance of the device.

The voltage V_{fd} can be determined by several methods. In this work we used the I-V curves where the current, for voltages greater than V_{fd}, depends exponentially with voltage due to field enhanced emission. For that reason, V_{fd} is determined as the voltage where a linear region in a semi-logarithmic graphic of the I-V curve appears.

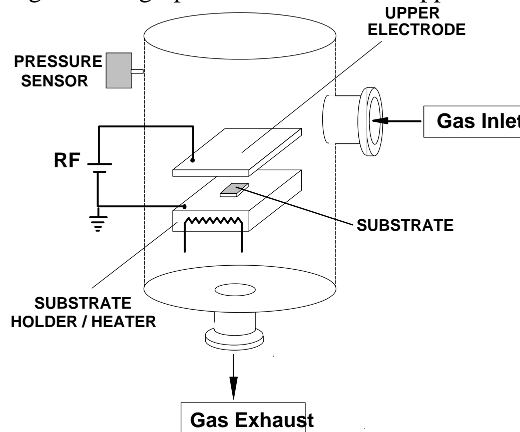

Fig. 1 Schematic diagram of reactor No. 1 used for process PA1.

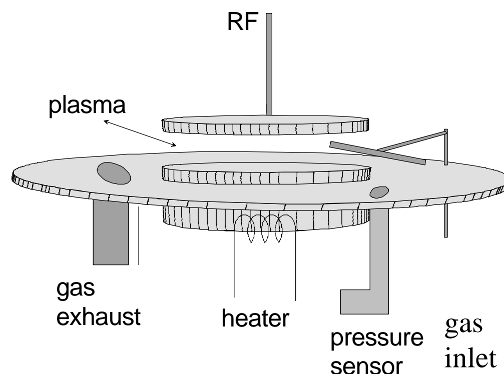

Fig. 2 Schematic diagram of reactor No. 3 used for processes PA1 and PA2.

To compare with results previously reported for other high deposition methods, we will also use the crystalline-like approximation where:

$$V_{fd} = \frac{q}{2 \cdot \varepsilon_0 \cdot \varepsilon_i} \cdot N_o \cdot d_i^2 \ . \qquad (1)$$

q is the electron charge; ε_0, ε_i are the absolute and relative dielectric constant respectively; d_i is the intrinsic film thickness; and N_o is a density of ionized deep states when electron emission equals hole emission.

To characterize the quality of the films we determined the position of the Fermi level E_{F0} using the I-V-T curves of the PIN diodes. If a measurement of the steady state current for a given voltage at different temperatures is made, the activation energy obtained from these curves should correspond to E_C-E_{Fq}, where E_{Fq} is the quasi-Fermi level. If however, the current is measured for each temperature with a time delay of 1 s after bias, the thermal generation current will exceed its steady state value and the activation energy will correspond to E_C-E_{F0} [8].

3. Results and discussions

A deposition rate of 2.5 μm/hr for a-Si:H layers was obtained in 3 different reactors using parallel electrodes of equal area, long gas residence and optimizing the other deposition parameters to 20 sccm of SiH_4, 43 Pa, 50 mW/cm^2 and 200 ^{o}C.

The deposition rate obtained in Ref. [6] was increased to 1.5 μm/hr with the addition of parallel electrodes of equal area .

The gap E_g was determined by transmittance, obtaining values within the interval 1.7-1.75 eV, for all films using both processes.

The presence of SiH bonds was determined through the absorption peaks around 640 cm^{-1} and 2000 cm^{-1}. The presence of. SiH2 bonds, through the absorption peaks around 850 and 2090 cm^{-1}. The selected deposition regime, reveled a small amount of high order SiH_n radicals, as indicated by the FTIR measurements.

Diodes with thickness of 8 and 18 μm fabricated with the process PA1 reached full depletion voltage at 60 V and 220V respectively, giving a constant density of charged states of 10^{15} and $8x10^{14}$. In Table 1, these results are compared to results previously reported. As can be seen, the two new high deposition methods produce similar values of N_o as previously reported for deposition at 80 MHz and dilutions of silane in He.

Diodes 3 μm thick fabricated with process PA2 reached full depletion at 8 V producing a constant density of charged states of No=1.2×10^{15} cm^{-3}.

The I-V curves for diodes with thickness of 3, 8 and 18 μm are shown in Fig. 3, where $V_{norm}=V/V_{fd}$ for each device, is plotted along the x-axis. As can be seen, the current in the three cases starts to depends exponentially with the voltage at V_{norm}=1,.

In I-V-T experiments, devices were fixed at a given temperature and I-V curves were measured with a time delay of 1 s. Fig. 4 presents the curves I vs 1000/T for reverse voltages starting from V_D=-50 V to V_D=-250 V with steps of 50 V for a typical device prepared with process PA2.

Table 1. Values of deposition rate and charged density of states for several deposition processes.

Deposition Process	Dep. rate [μm/hr]	N_o [cm^{-3}]
Standard SiH_4 [4]	1	$1.28x10^{15}$
SiH_4 in He [3]	2.88	$1.7x10^{15}$
PA2	2.5	$<10^{15}$
PA1	1.5	$1.2x10^{15}$

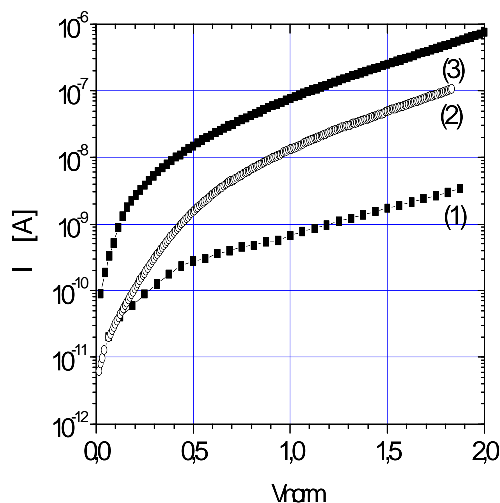

Fig. 3. log I_D vs V_{nom} curves (1), (2) and (3) for devices 3, 8 and 18 μm thick under reverse bias. $V_{nom}=V/V_{fd}$,.

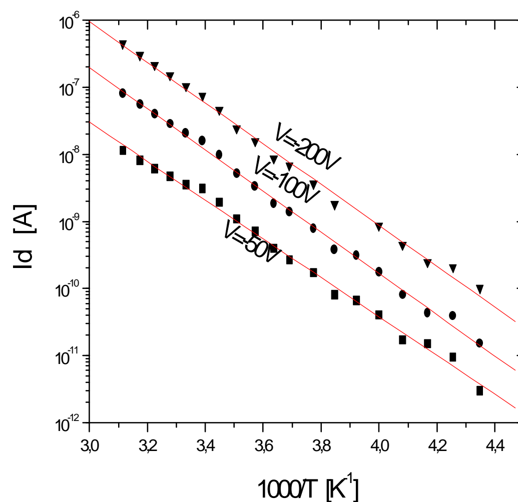

Fig. 4. I vs 1000/T curves of an 18 μm thick device, for voltages between –50 V (curve (1)) and –250 V (curve (5)), in steps of –50 V.

The slope for these curves in the temperature range between –45 and 45 ^{o}C and for all the devices examined, remains practically independent of the voltage, giving an average activation energy in the order of 0.65 eV, which also points to the fact that the Fermi level in equilibrium for these devices is in the order of 0.2 V above the middle of the gap as expected.

4. Conclusions

The deposition rate of 0.9 μm/hr previously obtained for a gas mixture of 10% SiH_4 in H_2 at 300 ^{o}C, 66.7 Pa, rf power of 50 mW/cm^2 and flow rates of 150 sccm, with a gas injector, was increased to 1,5 μm/hr by changing the

parallel non-symmetric electrodes to electrodes of equal areas.

The electrical characterization of thick PIN diodes fabricated with processes PA1 and PA2 demonstrates that the new deposition processes developed to duplicate the deposition rate of the films, provided a constant density of charged states similar to the values reported for standard deposition methods or for high deposition rate using SiH_4 diluted in He. The Fermi level was determined very close to the expected value at 0.65 eV below the conduction band.

Acknowledgments

The authors acknowledge Olga Gallego M. I. Alayo and C. A. Villacorta for sample preparation. This work was financially supported by CONACYT projects 28092A, 3192P-A9607 and FAPESP project # 96/ 7183-6

References

[1] R.L. Weisfield, Proc. IEDM, San Francisco, 1998
[2] W. Hong, A. Mireshghi, J. Drewery, T. Ying, Y. Kitsumo, S. Kaplan and V. Perez-Mendez, IEEE Trans. Nuclear Sci., **42**, 240(1995).
[3] T. Pochet, A. Ilie, A. Brambilla and B. Equere, IEEE Tran on Nuc. Sci. **41**, 1014(1994).
[4] R. Curtins, N. Wyrsch and A.V. Shan, Electronics Letters, 23, 228(1987).
[5] S. Will, H. Mell, M. Poschenrieder and W. Fuhsm, Proceedings of the “17th Inter. Conf. on Amorphous and Microcrystalline Semiconductors”, Budapest, Hungary, 25-29 August, 1997 , p. 131.
[6] S. Soto, M. Estrada, A. Merkulov and R. Asomoza, Thin Solid Films **330**, 83(1998).
[7] M. Estrada, and I. Pereyra, Thin Solid Films, **346**, 255(1999).
[8] R.A. Street, Appl. Phys. Lett **57**, 1334(1990).