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Authors
Hong, W.S.
Mireshghi, A.
Drewery, J.S.
et al.

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Lawrence Berkeley Laboratory
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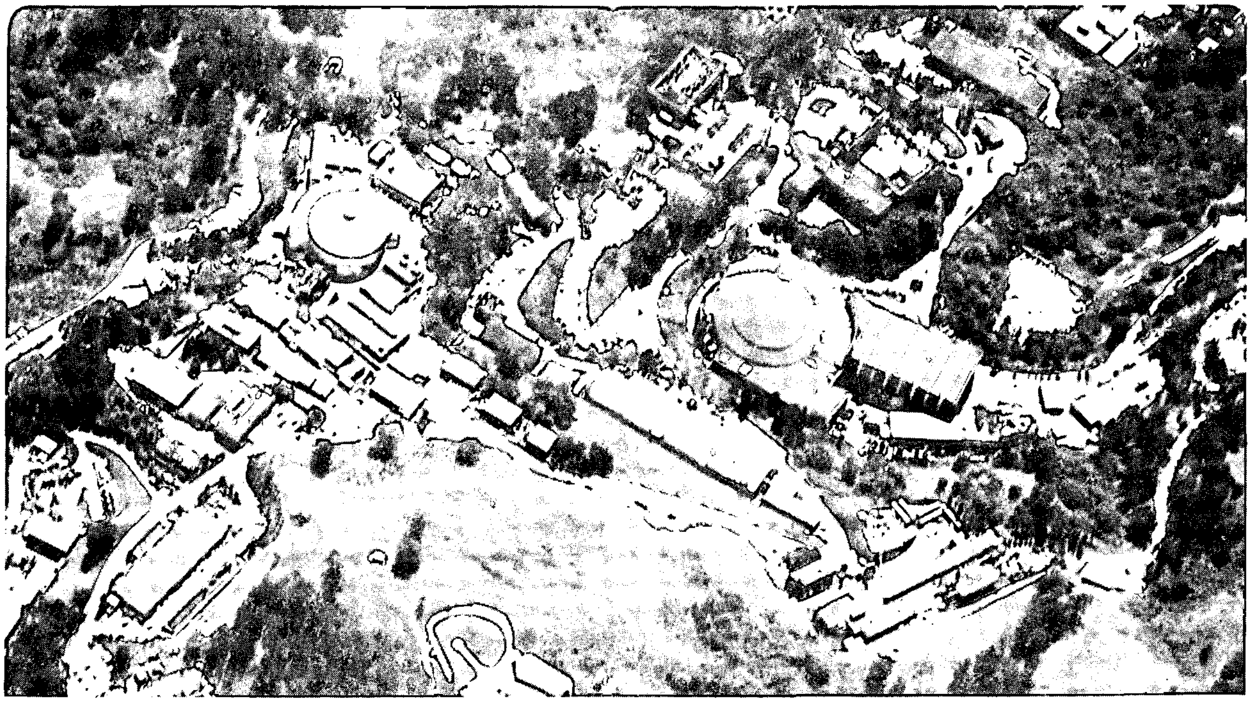
November 1994



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Wan-Shick Hong, Ali Mireshghi, John S. Drewery, Tao Jing, Yu Kitsuno,
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Physics Division
Lawrence Berkeley Laboratory
University of California
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Charged Particle Detectors Based on High Quality Amorphous Silicon Deposited with Hydrogen or Helium Dilution of Silane

W.S. Hong, A. Mireshghi†, J.S. Drewery, T. Jing, Y.Kitsuno*, H. Lee, S.N. Kaplan,
and V. Perez-Mendez
Physics Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720, U.S.A.
†Sharif University of Technology, Tehran, Iran
*Chemicals Research Laboratory, Showa Denko K.K., Kawasaki, 210 Japan

Abstract

Electrical transport properties of our PECVD a-Si:H material has been improved by using hydrogen and/or helium dilution of silane and lower substrate temperature for deposition. For hydrogen-diluted material we have measured electron and hole mobilities ~4 times larger, and $\mu\tau$ values 2-3 times higher than for our standard a-Si:H. The density of ionized dangling bonds (N_D^*) also showed a factor of 5-10 improvement. Due to its higher conductivity, the improved a-Si:H material is more suitable than conventional a-Si:H for TFT applications. However, it is difficult to make thick layers by H-dilution because of high internal stress. On the other hand, thick detectors can be made at a faster rate and lower stress by low temperature deposition with He-dilution and subsequent annealing. The internal stress, which causes substrate bending and delamination, was reduced by a factor of 4 to ~90 MPa, while the electronic quality was kept as good as that of the standard material. By this technique 35 μm-thick n-i-p diodes were made without significant substrate bending, and the electronic properties, such as electron mobility and ionized dangling bond density, were suitable for detecting minimum ionizing particles.

I. INTRODUCTION

Applications of hydrogenated amorphous silicon (a-Si:H) photodiodes for solar cells is already in the industrial phase now, and the objective of most related research work in the photovoltaic field is to improve the quality of the material, to achieve higher efficiency, and also to increase deposition rate for economic reasons. Radiation detection applications of a-Si:H are also well established. Various topics of interest, such as charge collection, signal generation, and noise reduction are addressed in the literature.[1] Current research efforts are mostly directed towards the improvement of electronic transport characteristics[2], deposition at higher rate[3], reduction of internal stress[3], and fabrication of large area pixel array detectors for real time X-ray and gamma ray imaging applications.[4] Major a-Si:H detector characteristics, such as speed, charge collection efficiency, and signal to noise ratio are defined by the electrical parameters of the material, namely mobility (μ), mobility life time product ($\mu\tau$), and ionized defect density (N_D^*). In this paper we will discuss our new results on the improvement of these parameters by hydrogen or helium dilution of silane, which is the main process gas in the plasma enhanced chemical vapor deposition (PECVD) technique.

For X-ray and γ-ray detection, thin a-Si:H n-i-p photodiodes can be coupled to CsI(Tl) scintillator layers of 100-1000 μm in thickness with induced columnar structure for enhanced spatial resolution.[5] For charged particles, especially the minimum ionizing particles (MIP), n-i-p diodes with thick (> 50 μm) i layers are required to produce sufficient e-h pairs in the intrinsic layer. However, it is possible to use the scintillator-photodiode configuration for charged particles as well, if thin n-i-p diodes are to be used.

II. PROPERTIES OF N-I-P DIODES

Amorphous silicon n-i-p diodes are produced by successive deposition of n-doped, intrinsic, and p-doped layers on Cr or ITO coated substrates in a plasma enhanced CVD reactor. The i layer is the sensitive part and is depleted under appropriate reverse bias. The collected electron and holes, arising from the interaction of the incident radiation in this region generate a signal which is picked up by a charge sensitive pre-amplifier. The signal response as a function of shaping time can be calculated from the mobility and the electric field in the i layer at a given bias.

The required thickness of the i layer depends on the application. For minimum ionizing particles(MIP) a thickness of about 50 μm is required, since 80 electron-hole (e-h) pairs per micron are produced on the average from minimum ionizing particles[6]. In a pixel array configuration with a typical pixel size of ~ 300 μm and diode thickness of 50 μm, the generated signal (~ 4000 e) would be about 20 times larger than the noise.

The electric field profile inside the i-layer is given by the Poisson equation:

$$\frac{d^2\Phi(x)}{dx^2} = -\rho = -\frac{qN_D^*}{\varepsilon_o\varepsilon_{aSi}}$$

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where $\Phi(x)$ is electric potential, ρ is electric charge density, ε_o is the dielectric constant of vacuum and ε_{aSi} is the relative dielectric constant of a-Si:H. The full depletion bias, V_f, is obtained as follows with the boundary conditions of $\Phi(0) = V_f$ and $\Phi(d) = 0$ where d is the i-layer thickness.

$$V_f = \frac{q N_D^* d^2}{2 \varepsilon_o \varepsilon_{aSi}}$$

Therefore, the magnitude of the applied bias necessary for depletion of the i layer varies linearly with the ionized defect density (N_D^*) and is proportional to the square of the i layer thickness. For a 50 μm thick diode, with an ionized defect density of $5 \sim 7 \times 10^{14}$ cm^{-3}, full depletion can be achieved at a minimum voltage of 1300 V. In a normal diode with doped layer thickness of 2-3 nm, application of such a large bias will result in a strong electric field at the p-i interface near the electrode, which in turn will trigger some breakdown mechanism. The peak field in the p-i interfaced can be sufficiently moved away from the contact region by increasing the thickness of the p layer to 20-30 nm as illustrated in Fig.1(a). The depletion of the diode can be further promoted by depositing a thin p-layer in the middle of the intrinsic layer (see Fig. 1(b)). This layer will reduce the required depletion voltage approximately by a factor of 2.[1] However, the p layer is expected to act as traps for electrons. In Fig.2, the electron collection efficiency, defined as the ratio of the number of electrons before and after passsing the buried p-layer, is calculated for a hypothetical structure of a 50 μm-thick diode having one p-layer in the middle, and is plotted for various doping densities of the buried layer. As shown in this figure, the electron loss for an effective doping density as high as 3×10^{16} atoms/cm^3 is not significant.

III. ALTERNATIVE PRODUCTION METHOD

Conventional a-Si:H is produced at RF frequency of 13.56 MHz, with pure silane as the main process gas. Below we will discuss alternatives to this standard recipe, each providing certain advantages in terms of the growth rate and quality of the deposited material.

A. Higher RF Frequency

Higher PECVD deposition rate of intrinsic a-Si:H films required by commercial applications such as, low cost solar cells and production of thick detectors, can be achieved by the use of higher plasma excitation frequencies, in the Very High Frequency (VHF) band (30-300 MHz). Application of excitation frequencies in the 10-110 MHz range has shown to have no deterioration effect on the electronic properties of the deposited film.[3,7] We have adopted this method and currently we are depositing our a-Si:H films at 85 MHz. At this frequency, the deposition rate of standard a-Si:H films has increased to 2.3 μm/hr., while it is ~0.7 μm/hr. at 13.56 MHz.

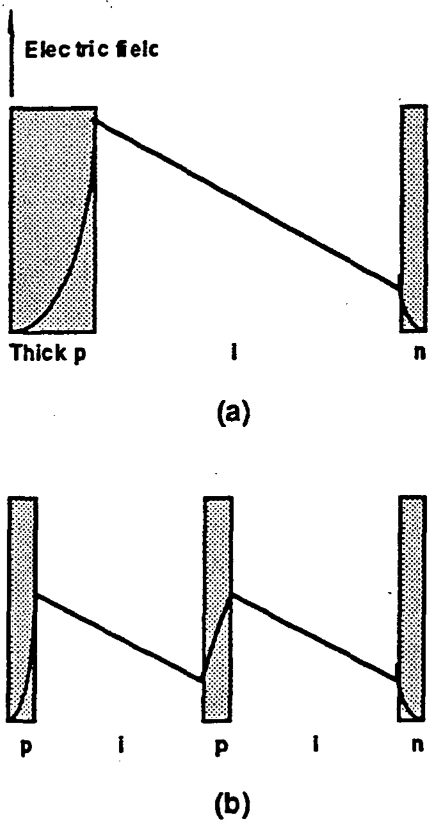


Fig. 1 Full depletion schemes: (a) thick p layer, (b) buried p layer

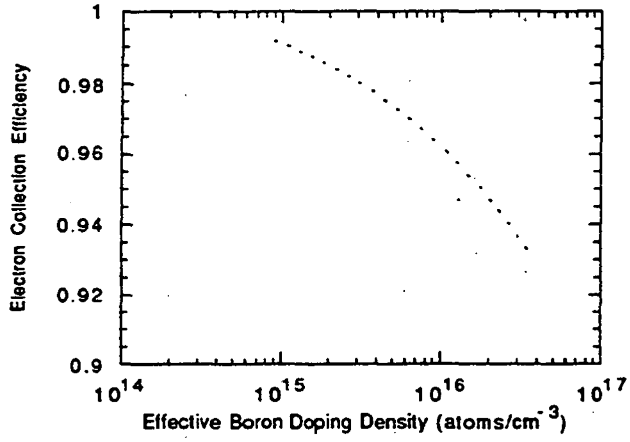


Fig. 2. Calcultated electron collection efficiency as a function of the effective doping density of the buried p-layer in a 50 μm thick detector at a fixed bias of 700V.

B. Hydrogen Dilution of Silane

Our measurement results on n-i-p diodes produced under various hydrogen to silane ratios show significant improvement in the electronic transport properties of the material deposited with hydrogen dilution.[8,9] Our findings are quite consistent with the results of others groups[10-13], who have reported improved photovoltaic characteristics in their a-Si:H solar cells, as a result of hydrogen dilution, both at initial and light degraded state. We have investigated the effect of hydrogen dilution at different RF power densities and substrate temperatures. The deposition parameters are given in Table I. The optimum results are obtained at a hydrogen to silane gas ratio of 15, RF power density of 60 mW/cm^2 and substrate temperature of 190°C. We measured mobility (μ), mobility lifetime product ($\mu\tau$), density of ionized dangling bonds (N_D^*), and internal stress of many samples. For μ and $\mu\tau$ measurements, we used the standard time of flight (TOF) technique. In this technique, the transit time of a packet of e-h charges produced by a laser pulse at one end of a n-i-p diode and collected on the other end is determined from generated phototransient current pulses.[14] The measured electron and hole mobilities are about 3-4 times larger than our standard a-Si:H values (Table II). The $\mu\tau$ values also improved by a factor of ~ 2 for the hydrogenated samples.

For N_D^* we used hole onset measurement, in which the hole signal amplitude is measured while illuminating the n side of an n-i-p diode at various applied bias voltages. The hole signal threshold bias corresponds to full depletion of the i layer and used to calculate the value of the N_D^* as discussed in section II.[15] In Fig. 3 the calculated electric field profiles in a 70 µm-thick n-i-p diode are shown for two hypothetical N_D^* values of 3×10^{14} cm^{-3} and 7×10^{14} cm^{-3}. The measured values of N_D^* for the hydrogenated material are more than 10 times lower than for our standard a-Si:H. As hydrogen to silane mixing ratio is increased from the optimum value of 15, some degrees of crystallinity is observed. We have used a simple macroscopic model to show that even with the existence of the microcrystalline phase, at the low compositional fractions in some of our samples, the increase in the mobility values result predominantly from improvement in the quality of the amorphous phase.[9] The samples deposited with hydrogen dilution are, on the average, under stronger internal stress (~2 times) compared to the normal a-Si:H samples (see Table II).

Table I. Deposition Conditions for the Intrinsic Layers of Hydrogen-diluted Samples

Samples	$[H_2]$ / $[SiH_4]$	Temp. (°C)	Power Density (mW/cm^2)	Deposition Rate (µm/hr.)
MC361	15	190	60	1.4
MC362	15	190	90	1.5
MC363	15	250	60	1.1
MC292	20	190	60	0.8
MC370	20	190	90	0.8
MC354	20	250	60	0.8
std. a-Si:H	0	250	50	2.3

Table II. Measured Electron and Hole Transport Parameters and Stress

Samples	μ_e (cm^2/V•s)	$(\mu\tau)_e$ (cm^2/V)	μ_h (cm^2/V•s)	$(\mu\tau)_h$ (cm^2/V)	N_D^* (cm^{-3})	Stress (MPa)
MC361	4.2	2.2×10^{-7}	0.013	6.0×10^{-8}	2×10^{13}	650
MC362	2.7	1.1×10^{-7}	0.009	3.4×10^{-8}	9×10^{13}	680
MC363	1.2	1.2×10^{-7}	0.006	1.7×10^{-8}	3×10^{13}	610
MC292	2.5	3.0×10^{-7}	0.011	1.7×10^{-8}	1.6×10^{14}	650
MC370	1	1.4×10^{-7}	0.009	2.0 x 10-8	1.4×10^{14}	580
MC354	1.1	1.5×10^{-7}	0.003	2.0×10^{-8}	1.3×10^{14}	720
std. a-Si:H	1.2	1.2×10^{-7}	0.004	2.6×10^{-8}	7×10^{14}	350

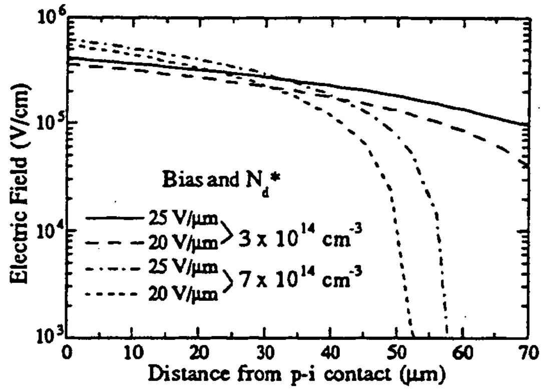
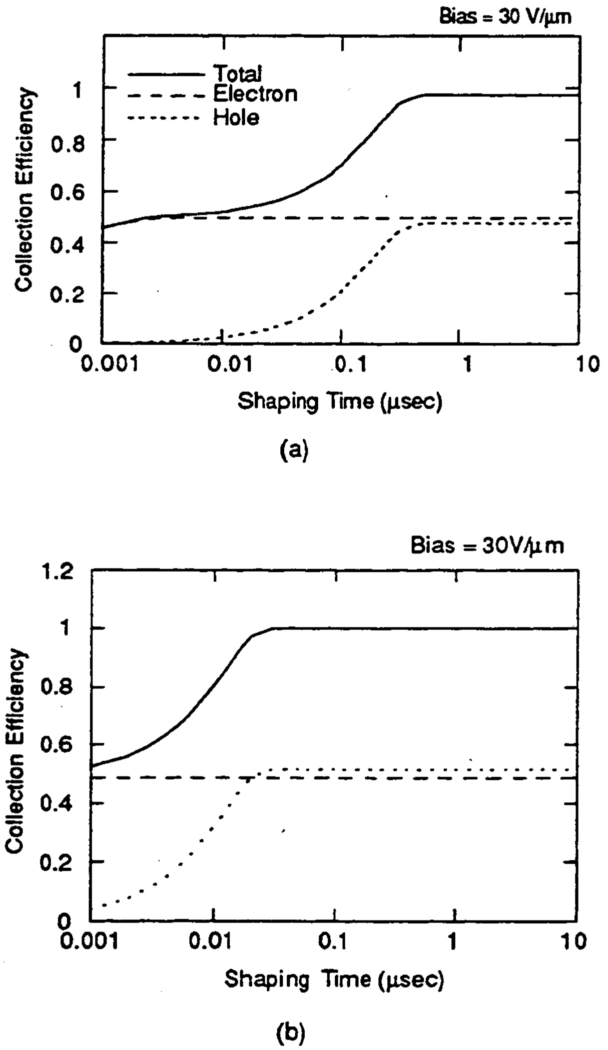


Fig. 3 Electric field in i-layer of a-Si:H n-i-p diode calculated for two different biases and ionized dangling bond densities



(a)

(b)

Fig.4 Normalized electron and hole collection efficiency for 1 μm thick n-i-p diodes (a) standard a-Si:H (b) hydrogen diluted sample

The signal response as a function of shaping time can be calculated from the mobility and the electric field in the i-layer at a given bias. Fig. 4 shows the signal from electrons and holes for thin (1 μm) detector diodes made by conventional method and by hydrogen dilution, respectively. The parameters used in this calculation are: $\mu_e = 1$ cm^2/V•s, $\mu_h = 0.005$ cm^2/V•s, $\tau_e = 9 \times 10^{-8}$ sec., $\tau_h = 3 \times 10^{-6}$ sec. for standard a-Si:H, and $\mu_e = 4$ cm^2/V•s, $\mu_h = 0.01$ cm^2/V•s, $\tau_e = 5 \times 10^{-8}$ sec., $\tau_h = 5 \times 10^{-6}$ sec. for H_2-diluted samples. Fast timing for both is achieved by collecting the full electron signal only in < 5, 0.08 nsec., respectively. Since both the mobility and lifetime are larger in the H_2-diluted diode, the shaping time for full charge collection can be greatly reduced.

C. *Helium Dilution of Silane*

It has been reported that the deposition rate of the amorphous silicon film can be increased by mixing silane with helium, and the "He-diluted" n-i-p diode can be used to detect a-particles.[16] However, the N_D^* in the He-diluted i-layer was about 2 times larger than that in the standard a-Si:H materials. We modified the deposition parameters and achieved both a moderate enhancement in the deposition rate and a reduction in the N_D^*. At 85 MHz, the growth rate of the film deposited with 60% SiH_4 - 40% He mixture increased to 3.5 ~ 4 μm/hr. and the N_D^* was reduced to 2.5×10^{14} cm^{-3}. The deposition parameters are summarized in Table III.

This result of lower N_D^* and higher deposition rate indicated a method to make thick films of good quality at a lower internal stress state. If we lower the growth temperature, the film stress will decrease and the N_D^* will increase.[17,18] However, for standard a-Si:H films, the increased N_D^* can be mostly recovered by annealing at a proper temperature without affecting the stress appreciably.[19] In Fig.5, relaxation of spin density with annealing time was plotted for standard a-Si:H diodes which were degraded and annealed at different temperature. At 160°C, the spin density was reduced by a factor of 5 after ~80 hours and underwent little change with further heat treatment. Based on this result, we deposited 5 to 35 μm-thick p-i-n diodes with He-dilution at 150°C instead of 250°C, and annealed them at 160°C for 100 hours or longer. Material properties of the as-deposited and annealed films are listed in Table IV.

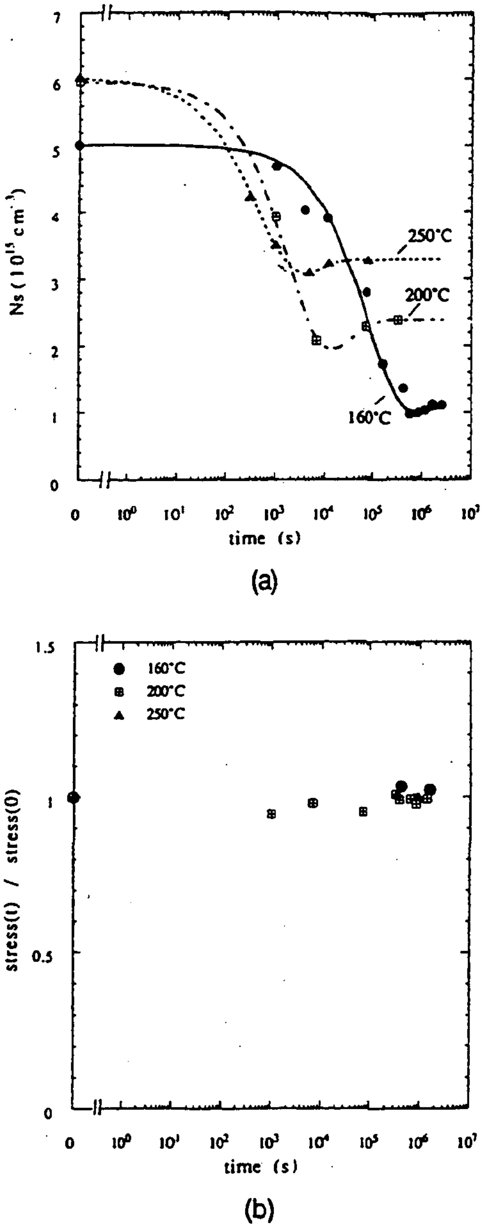
The stress of as-deposited films was around 90 MPa, which is one-fourth of that of the standard films, and the N_D^* was 3×10^{15} cm^{-3}. After annealing, the N_D^* decreased to 7×10^{14} cm^{-3}, which is low enough for detector applicaiton, and the stress remained virtually unchanged(~100 MPa). The μ_e and $(\mu\tau)_e$ values are 1 cm^2/V•s and 1×10^{-8} cm^2/V, respectively, and changed only slightly with annealing. In Fig.6, the relationship between stress and dangling bond density before and after the heat treatment is plotted for He-diluted samples deposited at various temperatures. The curves are shifted downward, but not to the left, after annealing and the reduction of N_D^* is more pronounced for samples deposited at low temperatures.

For comparison, a-Si:H from pure SiH_4 gas was deposited at 150°C and annealed at 160°C. The stress and N_D^* values of the as-deposited samples from pure silane are similar to those of He-diluted samples made at 150°C. However, the N_D^* reached only 1 x 10^{15} cm^{-3} after annealing. The stress did not change with annealing in all cases. It is implied from this result that the low temperature deposition only lowers the internal stress and the He-dilution facilitates the material to restore low defect densities. Therefore, the He-diluted films prepared by low-temperature deposition and subsequent annealing are suitable for thick detectors since they have lower film stress and faster deposition rate than standard a-Si:H and electronic qualities comparable to those of the standard films.

IV. APPLICATIONS

A-Si:H charged particle detectors are adaptable to a variety of applications. One example is the detection of MIPs in high energy physics research. As discussed in section II, n-i-p diodes of thickness >50 μm are required to have an adequate signal. In the past, we have made n-i-p detectors as thick as 63 μm[20]. However, production of such thick detectors has been difficult due to considerable internal stress and low deposition rate. These problems can be circumvented largely, by helium dilution of silane, as addressed in this paper.

Two dimensional arrays of a-Si:H n-i-p diodes are good candidates for β-radio-chromatography applications. A radio-chromatogram consists of a column along which separation of components of a labeled mixture is possible by detecting the position and concentration of a series of spots or bands produced by accumulation of different component. Normally, β-emitters such as ^3H ($E_{\beta\ max}$ =18 KeV), ^{14}C ($E_{\beta\ max}$ =150 KeV), and ^{32}P ($E_{\beta\ max}$ =1.7 MeV) are used for labeling the mixtures. In a two dimensional scheme, a number of mixtures can be analyzed simultaneously, by using more columns on a chromatogram. The spots can be measured by X-ray films with very good spatial resolution. However, the film processing is time consuming. For a real time analysis, a-Si:H pixel arrays have advantage of higher spatial resolution over the alternative systems such as multiwire proportional chambers (MWPC) and scintillating optical fibers.[21] Silicon strip detectors with comparable spatial resolution (SSD) have also been suggested for this application.[22]



(a)

(b)

Fig. 5 Time dependence of (a) spin density and (b) normalized residual stress during annealing at different temperatures. The samples were degraded by heating at 300°C for 10 minutes and quenched in water prior to annealing. The stress values are normalized to the stress of as-deposited sample.

Table III. Deposition Parameters for He-diluted and Undiluted a-Si:H

Gas	Temp.(°C)	Power Density (mW/cm^2)	Pressure (mTorr)	Deposition Rate (μm/hr.)
100% SiH_4	250	40	300	2.3
60% SiH_4-40% He	250	90	500	3.5~4

Table IV. Measured Electron Transport Parameters and Stress

Samples	μ_e (cm^2/V•s)	$(\mu\tau)_e$ (cm^2/V)	N_D^* (cm^{-3})	Stress (MPa)
standard a-Si:H (deposited at 250°C)	1.2	1.2×10^{-7}	7×10^{14}	350
standard a-Si:H (deposited at 150°C)				
as deposited		1×10^{-8}	2.5×10^{15}	80
annealed			1×10^{15}	80
He-diluted(deposited at 250°C)	1.2	3×10^{-8}	2.5×10^{14}	320
He-diluted(deposited at 150°C)				
as deposited	0.8	1×10^{8}	3×10^{15}	90
annealed	0.8	2×10^{8}	7×10^{14}	100

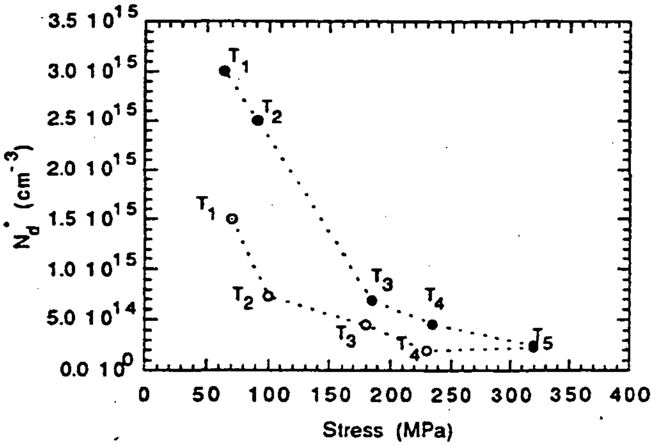


Fig. 6. Relationship between stress and ionized dangling bond density before and after annealing for He-diluted diodes. The deposition temperatures are: T_1 = 130°C, T_2 = 150°C, T_3 = 170°C, T_4 = 190°C, T_5 = 250°C

Thermal neutrons can also detected by a-Si:H n-i-p diodes interfaced with Gd converter. We have developed such detectors by vacuum coating ~2 µm Gd films on 20-30 µm thick a-Si:H diodes. Using a sandwiched structure with two layers of enriched Gd (in ^{157}Gd isotope) film coupled to n-i-p diodes, thermal neutron efficiencies of more than 60% are achievable.[23] Such detectors in a two dimensional configuration are excellent candidates for applications where high spatial resolution and good fast neutron and gamma rejection are desirable.

V. CONCLUSION

We have explored the effects of hydrogen and/or helium dilution of silane on various material properties of a-Si:H films. Hydrogen dilution enhanced the electronic properties of a-Si:H films at the expense of high internal stress. The optimum deposition parameters were found to be the H_2/SiH_4 mixing ratio of 15, substrate temperature of 190°C and power density of 60 mW/cm^2. The samples deposited under these conditions showed electron and hole mobilities ~4 times larger and $\mu\tau$ values ~2 times higher than those of standard a-Si:H materials. The ionized dangling bonds density was also reduced by a factor of 10, and thus full depletion of the detector could be achieved at a lower bias voltage. With higher carrier mobility in the intrinsic layer, the detector will have a faster response. Therefore, the H-diluted material is advantageous for use in large area two dimensional arrays, in which detector pixels can be integrated with TFT switches deposited by the same process and even read out by such TFT amplifiers.

Thick a-Si:H films for minimum ionizing particle detection can be made with low internal stress by deposition at low temperature with He-dilution and subsequent annealing to minimize substrate bending and delamination. 35 µm-thick films made by this technique showed internal stress of 100 MPa and N_D^* as low as 7 x 10^{14} cm^{-3} after annealing. The electron mobility and mt value of the He-diluted materials were comparable to those of conventional a-Si:H films. On the average, a minimum ionizing proton would produce 2800 electrons in the 35 µm-thick diode and the resulting signal to noise ratio would be 14 when the pixel size is 300 µm. The n-i-p diodes made by He-dilution can be used directly to detect minimum ionizing particles or be coupled to a Gd converter for thermal neutron detection.

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UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
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