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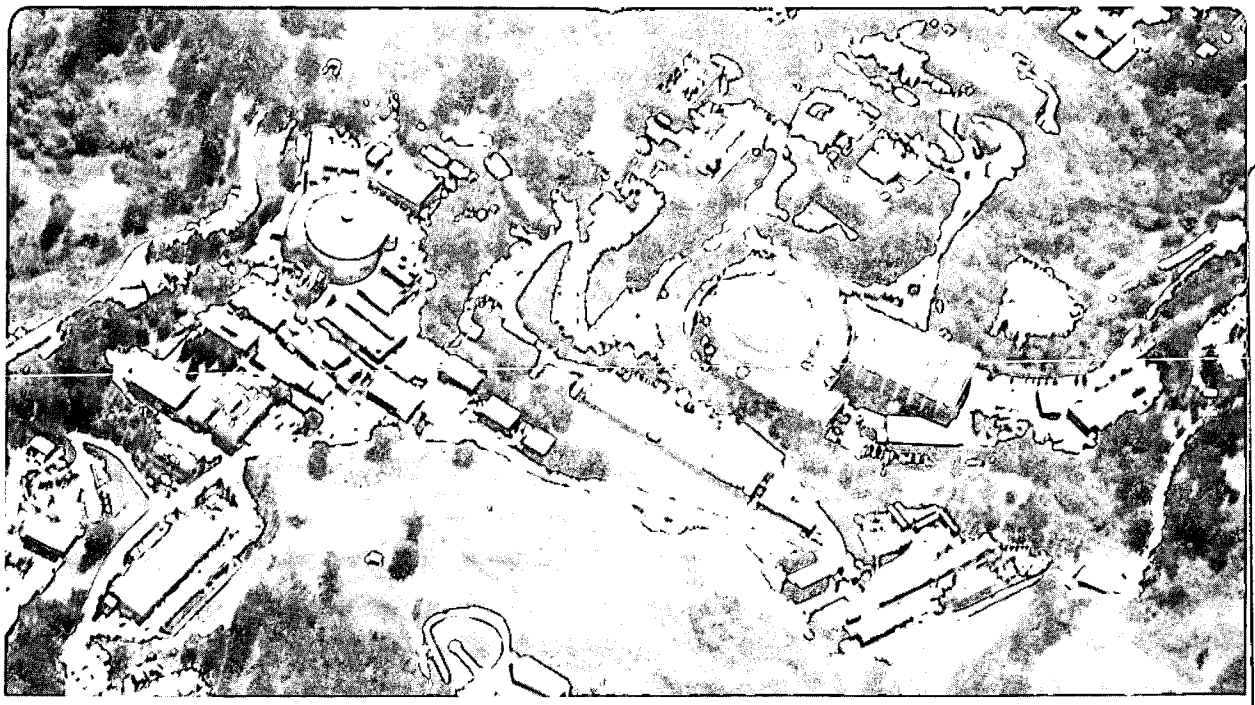

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THICK AMORPHOUS SILICON LAYERS SUITABLE FOR THE REALIZATION OF RADIATION DETECTORS

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ABSTRACT

Thick silicon films with good electronic quality have been prepared by glow discharge of He-diluted SiH_4 at a substrate temperature ~150°C and subsequent annealing at 160°C for about 100 hours. The stress in the films obtained this way decreased to ~100 MPa compared to the 350 MPa in conventional a-Si:H. The post-annealing helped to reduce the ionized dangling bond density from 2.5 x 10^{15} cm^{-3} to 7 x 10^{14} cm^{-3} without changing the internal stress. IR spectroscopy and hydrogen effusion measurements implied the existence of microvoids and tiny crystallites in the material showing satisfactory electronic properties. P-I-N diodes for radiation detection applications have been realized out of the new material.

INTRODUCTION

Thick (~50μm) hydrogenated amorphous silicon (a-Si:H) films have been drawing attention because of their potential advantages for the realization of large area charged particle detectors.[1, 2, 3] The deposition of thick, high quality layers by the established a-Si:H technology (glow-discharge of SiH_4 at $T_S \approx 250°C$) is handicapped by the high residual stress of such films, which causes substrate bending or film spallation.[4, 5, 6] However, the electronic quality of the low stressed material was reported to be poor.[7, 8]. Optimization of the deposition conditions and introduction of post-deposition steps helped us to overcome some of the difficulties. Our goal was to prepare films having: i) a high deposition rate, ii) residual stress, $\sigma \sim$ 100 MPa or less, iii) an ionized dangling bond density $N_d^* \sim 5 \times 10^{14}$ cm^{-3} or less and iv) mobility-lifetime product $\mu\tau$ of charge carriers of the order of $10^{-8} \sim 10^{-7}$ cm^2/V.

The following knowledge from the literature was a helpful guide to us on the way to overcome the above mentioned difficulties. The deposition rate was shown to increase when silane

is diluted with inert gas.[9, 10, 11] However, in many cases, adding inert gas to the plasma resulted in columnar morphology which degrades the transport characteristics.[12, 13] Among the various inert gases, helium was found empirically to have a minimal deterioration effect on the film quality.[14, 15] Therefore, we chose He as the dilution gas.

Lowering the substrate temperature was known to reduce the residual stress in films from values as high as 350 MPa down to ~100 MPa or even smaller.[3, 16] It was found that during such process a void-rich structure formed, which is capable of releasing the stress.[17] The as-deposited void-rich material, however, has poor electronic quality.[18] On the other hand, we have shown recently that annealing at temperatures lower than the deposition temperature can reduce the density of dangling bonds while the stress remains unchanged.[19]

In this paper we describe how we fabricated thick a-Si:H films with low residual stress and satisfactory electronic properties. We also present data revealing the structural changes appearing in the films under the new preparation condition.

EXPERIMENTAL PROCEDURES

Intrinsic layers with thicknesses of 5 ~ 50 μm were prepared by the plasma enhanced chemical vapor deposition (PECVD) technique at an excitation frequency of 85 MHz from a gas mixture of 40% SiH_4 - 60% He. The same gas mixture was also used for making thin p- and n-doped layers for fabrication of p-i-n diodes. Corning 7059 glass coated with thin (<200Å) indium tin oxide layer was used as a substrate. The substrate temperature was varied between 130°C and 250°C while all the other parameters were kept constant. Samples from pure silane were also deposited for comparison. Table I summarizes the deposition conditions for He-diluted and undiluted layers. Annealing at 160°C for 100 hours was applied to all samples.

Table I Deposition Parameters for Conventional and He-diluted Si films.

Gas	Temp.(°C)	Power Density (mW/cm^2)	Pressure (mTorr)	Deposition Rate (μm/hr.)
100% SiH_4	150, 160, 170, 190, 250	40	300	2.3
40% SiH_4-60% He	130, 150, 160, 170, 190, 250	90	500	3.5~4

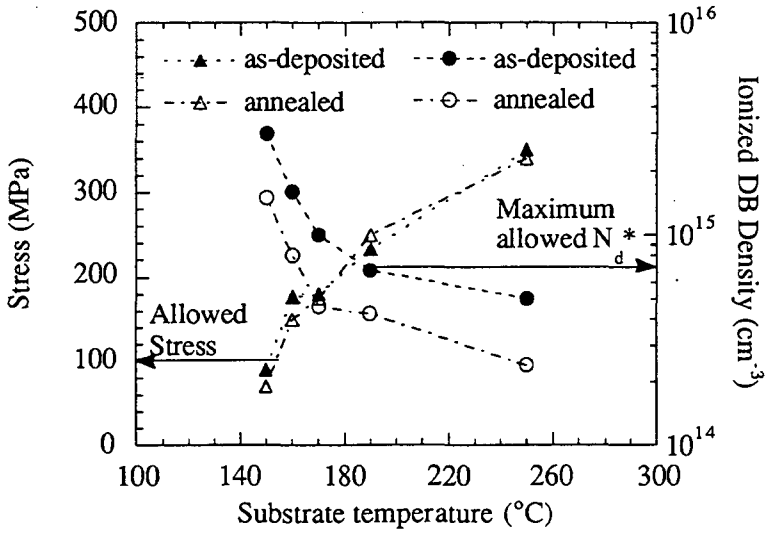


Fig. 1 Change in ionized dangling bond density (N_d^*) and residual stress with deposition temperature for standard samples. Closed and open symbols represent as-deposited and annealed samples, respectively.

The residual stress was determined by scanning the backside of the substrate with an Alphastep 200 profilometer and inserting the curvature in Stoney's equation.[20] The ionized dangling bond density, N_d^*, before and after annealing, was measured by the hole onset technique described elsewhere. [21] The electron mobility, μ_e, and mobility lifetime product, $(\mu\tau)_e$, were measured by the standard time of flight technique.[22] The vibrational spectra were detected by a FTIR Perkin-Elmer spectrometer in the range of 250-4500 cm^{-1} at a resolution of 4 cm^{-1}. The hydrogen desorption was measured with a home-made set up at a constant heating rate of 20°K/min. in the range between room temperature and 900°C.

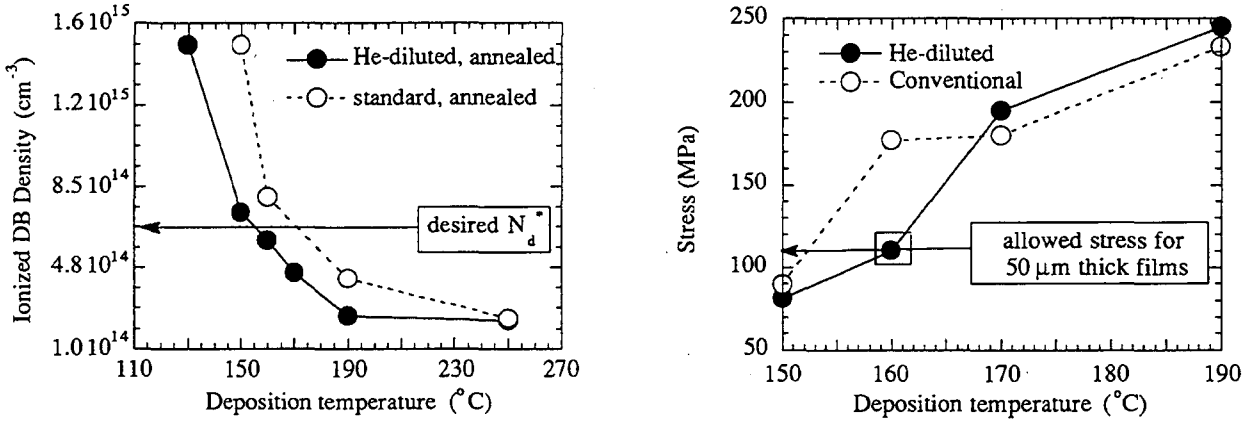


Fig. 2 (a) Change in ionized dangling bond density with deposition temperature for annealed samples, (b) Change in residual stress with deposition temperature

OPTIMIZATION OF THE DEPOSITION CONDITIONS

In Fig. 1 results are summarized[23] to show the effects of substrate temperature and post-annealing on the stress, σ, and the ionized dangling bond density, N_d^* for samples prepared from pure SiH_4. One observes clearly pronounced anti-correlation between the stress and the N_d^*. From this figure we also see that the post-annealing step affects significantly the N_d^* while the stress remains unchanged. Both the N_d^* and the stress experience strong gradients at substrate temperatures between 150°C and 200°C. In the same figure the desired values of the N_d^* and the stress for detector application are given by arrows. For the as-prepared samples it becomes clear from the figure that no deposition temperature provides films satisfying σ and N_d^* at the same time. Annealing improves the situation significantly, but at the cross-over point around 160°C the stress value is still higher than the desired value. For He-diluted samples a similar anti-correlation between σ and N_d^* is observed. The annealed and He-diluted samples show further quantitative improvement. This is demonstrated in Fig. 2.

In Fig. 2a the N_d^* vs. deposition temperature for He-diluted and conventional samples are compared. It is seen that with He-dilution the ionized dangling bond density is further reduced. Also the stress in the He-diluted samples is lower than in the conventional materials at ~160°C, as demonstrated in Fig. 2b.

Table II. Measured Electron Transport Parameters and Stress

Samples	μ_e ($cm^2/V \cdot s$)	$(\mu\tau)_e$ (cm^2/V)	N_d^* (cm^{-3})	Stress (MPa)
Standard (deposited at 250°C)				
as-deposited	1.2	1.2×10^{-7}	6×10^{14}	350
annealed	1.2		3×10^{14}	330
Standard (deposited at 150°C)				
as deposited	0.5	3×10^{-9}	2.5×10^{15}	90
annealed	0.5	7×10^{-9}	1.5×10^{15}	70
He-diluted(deposited at 250°C)				
as-deposited	1.2	3×10^{-8}	3×10^{14}	320
annealed	1.2		3×10^{14}	310
He-diluted(deposited at 150°C)				
as-deposited	0.8	1×10^{-8}	3×10^{15}	70
annealed	**0.8**	**2×10^{-8}**	**7×10^{14}**	**80**

In Table II the results of all four important electronic parameters for samples prepared at 250°C and 160°C with and without He-dilution, before and after annealing, are listed. Only the material prepared with He-dilution at 150°C and post-annealed for 100 hours provides a satisfying quality for realization of particle detectors.

STRUCTURAL DIFFERENCES BETWEEN THE CONVENTIONAL a-Si:H AND THE NEW FILMS

In Fig. 3 a typical FTIR transmittance spectrum of varous films is depicted. In addition to the stretching (s) band around 2000 cm^{-1} and the rocking (r) band at ~660 cm^{-1} which have been reported for high quality a-Si:H,[24] one clearly sees a doublet of modes around 850 cm^{-1} which correspond to the Si-H_2 and Si-H_3 bending (b) and wagging (w) region. Also, there is an additional band at ~500 cm^{-1}, which we assign to H-induced Si-Si vibrations. To the best of our knowledge, the latter has not been reported previously in the literature.

Fig. 4 shows an expanded plot of the Si-H_x stretching (fig.4a), Si-H_x bending (fig.4b) and the Si-Si:H (fig.4c) regions. Fig. 4a allows us to resolve the two peaks in the stretching region.

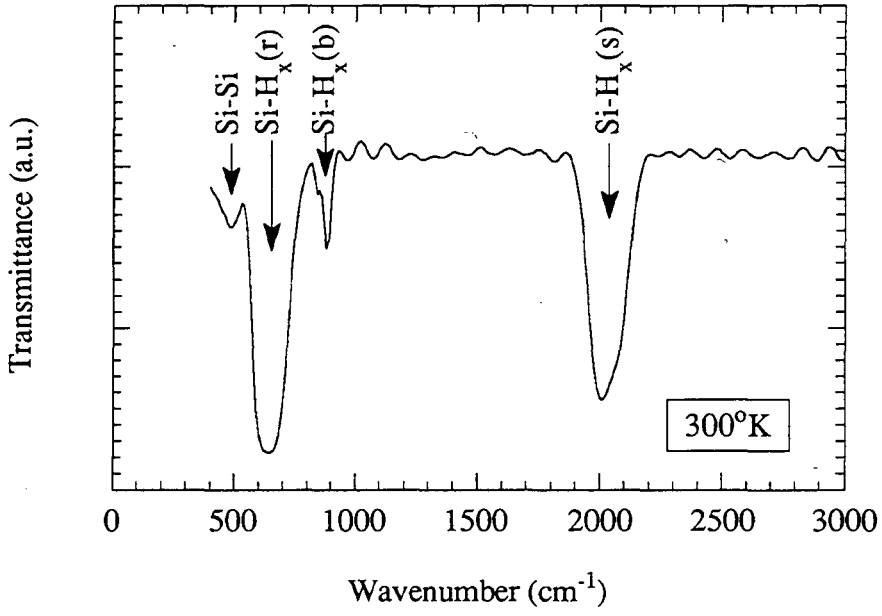
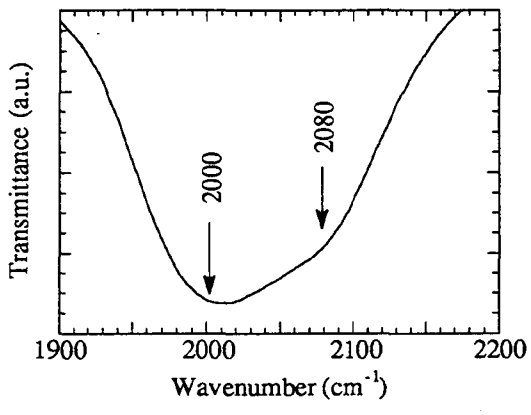
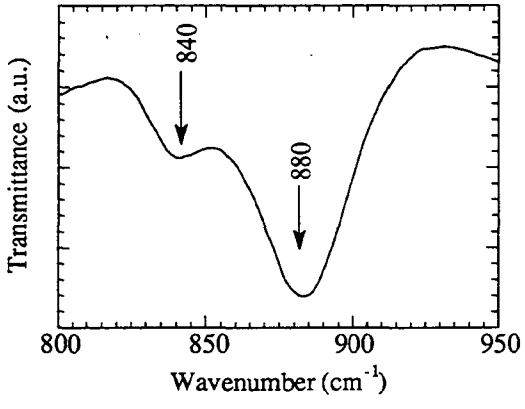


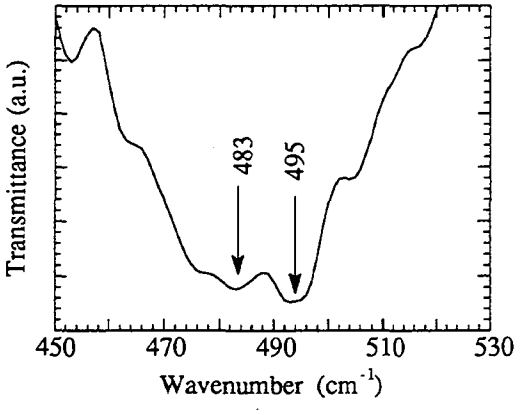
Fig. 3 FTIR transmittance spectrum of the He-diluted, low-temperature (150°C) deposited and post-annealed sample.



(a)



(b)



(c)

Fig. 4 Expanded FTIR spectra for the (a) stretching, (b) bending, and (c) Si-Si vibration region

The first broad peak around 2000 cm^{-1} is known to be due to vibration of the Si-H_1 bond in the interior of the amorphous network. The second one is shifted to higher wavenumber by ~80 cm^{-1}. Such shift is typical for the SiH_x vibration on the Si surface, as known from study of H-terminated c-Si monosurfaces.[25]. The appearance of this mode is a proof for the existence of voids in our materials. This is in agreement with the observation reported previously in the literature on low-temperature deposited a-Si:H films. The appearance of the scissor mode around 880 cm^{-1} in fig. 4b provides the information that our film contains a non-negligible amount of Si-H_2 bonds. The peak at 840 cm^{-1} is due to the existence of short $(Si-H_2)_n$ chains in the network on the void surfaces. The appearance of the mode at 500 cm^{-1} is a characteristic for the new films which we do not observe in the conventional a-Si:H. This spectrum is different from the typical Raman spectra reported for a-Si:H. There is a pronounced shoulder of this band in the region higher than ~500 cm^{-1}, which can be caused by the existence of tiny crystalline inclusion, covered by H, in the film. In this case the Si-Si transverse optical (TO) vibration can be induced by H and becomes observable in the IR-spectrum.

In Fig. 5, we show a typical hydrogen-effusion spectrum for the new samples. For comparison, also an effusion spectrum of conventional a-Si:H is shown. The high thermal stability of the He-diluted

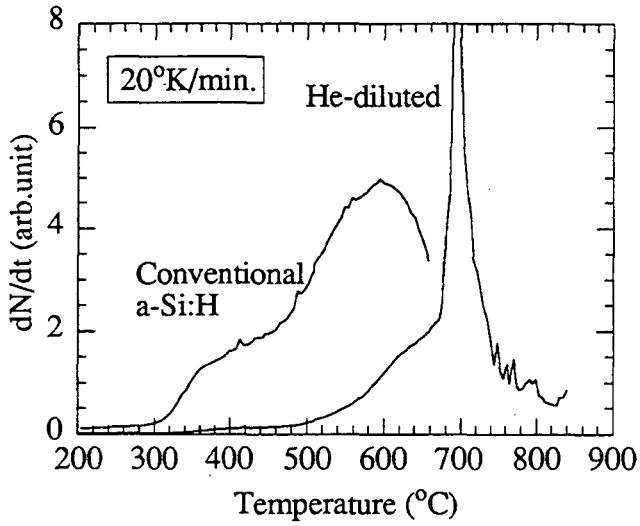


Fig. 5 Hydrogen effusion spectra of the conventional a-Si:H and of the He-diluted and low-temperature deposited sample.

material seen by a strong H-evolution peak at ~700°C is surprising. Usually, one expects the Si-H_2 bonds to decompose at ~400°C[26] More experiments need to be done to understand the unusual H desorption kinetics in this material.

CONCLUSION

We have been able to obtain a moderate increase in the growth rate to 3.5~4 μm/hr. and residual stress as low as ~100 MPa for films deposited at 150°C with He-dilution. Post-annealing at 160°C for 100 hours led to sufficiently low N_d^*(~ 7 x 10^{14} cm^{-3}). The combination of the low temperature growth, He-dilution and post-annealing of the film lends a way to produce a material that has a low residual stress and electrical properties satisfactory for thick (~50 μm) radiation detectors. The structure of the new film is seen to contain voids and tiny crystalline inclusions and is different from the one observed in conventional a-Si:H. A void-rich material is created here with satisfactory electronic quality, which is in contrast with previous conclusions in the literature. The high temperature stability of the hydrogen bonds remains an unresolved phenomenon.

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