

Preparation of highly photosensitive hydrogenated amorphous Si-C alloys from a glow-discharge plasma

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The preparation conditions for the deposition of hydrogenated amorphous silicon-carbon alloys (a -SiC:H) from a glow-discharge plasma have been systematically scanned by changing the starting-gas materials as well as the starting gas to hydrogen dilution ratio. A highly photosensitive alloy showing a photoconductivity to dark conductivity ratio of 10^7 at a band gap of 2.0 eV was prepared under optimized conditions.

Hydrogenated amorphous binary alloys such as hydrogenated amorphous Si-Ge and Si-C (a -SiGe:H and a -SiC:H) are attractive materials for application to solar cells, photoreceptors, and graphic devices, since their optical gap can be continuously controlled by changing the alloy compositional ratio.¹⁻³ However, in contrast to a -Si:H and a -SiGe:H, intrinsic a -SiC:H alloys prepared from a conventional glow-discharge decomposition technique have shown inferior photoelectric properties.^{4,5} This can be attributed to a higher density of dangling bonds which behave as recombination centers for photoexcited carriers. Recently, highly photosensitive a -SiGe:H alloys have been prepared from the glow-discharge plasma of $\text{SiH}_4/\text{GeH}_4$ mixtures using both a triode reactor and a H_2 -dilution technique.⁶⁻⁸ This was achieved through the control of the surface-growth process of a -SiGe:H leading to a denser network structure, i.e., a larger surface-diffusion coefficient of adsorbed radicals. This was realized by (1) the selection of less-reactive radicals using the triode reactor⁶ and by (2) the modulation of the surface coverage factor due to H atoms through H_2 dilution of the starting $\text{SiH}_4/\text{GeH}_4$ mixture.⁷

This communication describes the first successful preparation of highly photosensitive a -SiC:H using the same guiding principle (H_2 -dilution technique) which was used for the preparation of high-quality a -SiGe:H.

Table I shows the deposition conditions of a -SiC:H used in this experiment. Methane (CH_4), ethylene (C_2H_4), and monomethyl silane (SiH_3CH_3) were used for the carbon source, while only silane (SiH_4) was used for the silicon

source. Under these combinations, the influence of the sort of surface-impinging radicals (generated in plasma) on the properties of the resulting films was investigated. We assumed that the dominant radicals differ depending on the starting-gas material; namely, CH_x must be the main precursor in the plasma using CH_4 , C_2H_y in C_2H_4 , and SiH_wCH_z in SiH_3CH_3 , respectively. As the carbon content of the films increased from 0 to 0.35 (determined by secondary-ion mass spectroscopy), the optical band gap increased from 1.7 to 2.5 eV, and the band gap of 2.0 eV was obtained when the carbon content was approximately 0.16. A triode reactor was also used in the CH_4/SiH_4 system in order to investigate the influence of the reactivity of the radicals reaching the growing surface.

Figure 1 shows the dark conductivities and photoconductivities of a -SiC:H films prepared from the different methods as well as the various plasma conditions listed in Table I. As shown in the figure, the dark conductivities and photoconductivities of the films decreased with an increase in optical gap (E_0) determined from the $\sqrt{ah\nu} - h\nu$ plot, being in good agreement with the data reported by other groups^{9,10} and independent of starting-gas materials: CH_4/SiH_4 (circles), $\text{C}_2\text{H}_4/\text{SiH}_4$ (squares), and $\text{SiH}_3\text{CH}_3/\text{SiH}_4$ (triangles). This suggests that the film properties are not so strongly affected by the sort of radicals reaching the growing surface during the deposition. On the other hand, as shown in the figure (star symbols), the films prepared by the H_2 -dilution method show exceptionally high photoconductivities, although the deposition rate of the films is decreased

TABLE I. Deposition conditions of a -SiC:H films from glow-discharge plasma. sccm denotes standard cubic centimeter per minute.

Starting gas	Comp.	rf (13.56 MHz) power density (W/cm ²)	Flow rate (sccm)	Pressure (Torr)	T (°C)
$\text{CH}_4/(\text{CH}_4 + \text{SiH}_4)$ (diode + triode)	0-0.8	0.02-1	5	0.14	300
$\text{C}_2\text{H}_4/(\text{C}_2\text{H}_4 + \text{SiH}_4)$	0.2-0.7	0.5	5	0.05	300
$\text{SiH}_3\text{CH}_3/(\text{SiH}_4 + \text{SiH}_3\text{CH}_3)$	0.5-1	0.05-1	5	0.03	300
$\text{H}_2/(0.8\text{CH}_4 + 0.2\text{SiH}_4)$	10-50	0.01-0.1	11-51	0.2-1	300

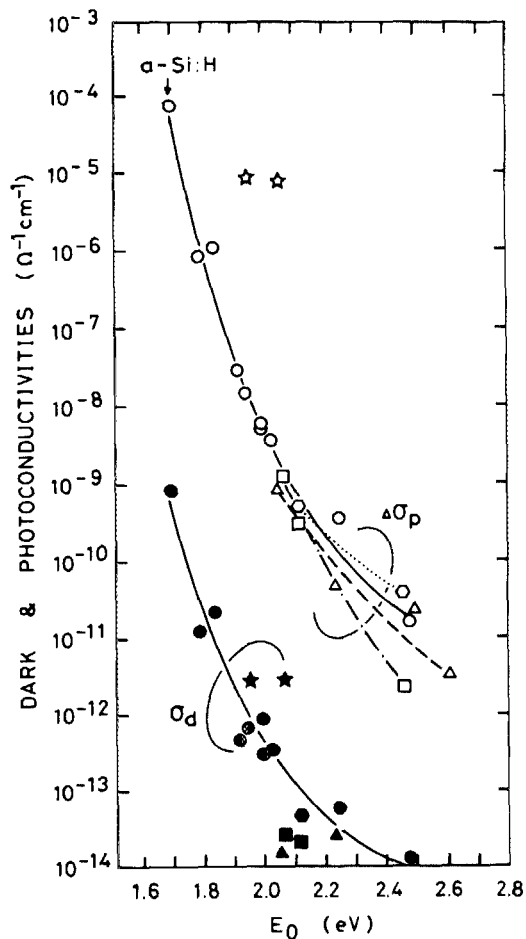


FIG. 1. Photoconductivity and dark conductivity of *a*-SiC:H prepared from a variety of deposition conditions plotted against their optical gap (E_0). Circles represent the conductivities of the films prepared from the CH_4/SiH_4 plasmas, squares— $\text{C}_2\text{H}_4/\text{SiH}_4$, triangles— $\text{SiH}_3\text{CH}_3/\text{SiH}_4$, and hexagons— CH_4/SiH_4 in a triode reactor.

($\sim 0.1 \text{ \AA/s}$) by 1 order of magnitude as compared to the other films. It is reasonable to speculate that the modulation of the growing surface by H impinging to the surface is the most important process for producing highly photosensitive *a*-SiC:H.

Figure 2 shows the refractive indices and the B values characterizing the optical absorption edge via $\sqrt{ah\nu} = B(h\nu - E_0)$ as functions of E_0 . Symbols used in the figure are the same as in Fig. 1. The refractive indices as well as the B values of all films deposited from nondiluted plasmas were smaller than those of the films prepared from the H_2 -dilution method. In other words, the films from the H_2 -dilution plasma have a higher density network and are structurally less disordered compared with the films prepared from the nondiluted methods. It should also be noted that B values of the films prepared using the triode reactor (triode film) are slightly improved, suggesting that the longer-lifetime radicals selected by the triode structure is favorable for the formation of a denser network, as is the case for *a*-SiGe:H. However, the positive effect (seen in the structural properties) realized using the triode reactor⁶ is partially negated in

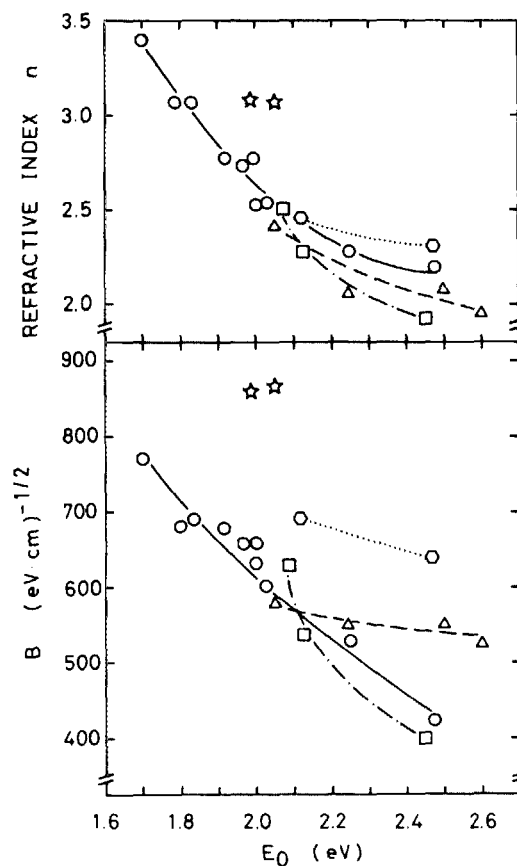


FIG. 2. Refractive index (top) and B value (bottom) of *a*-SiC:H plotted against optical gap. (Symbols same as Fig. 1.)

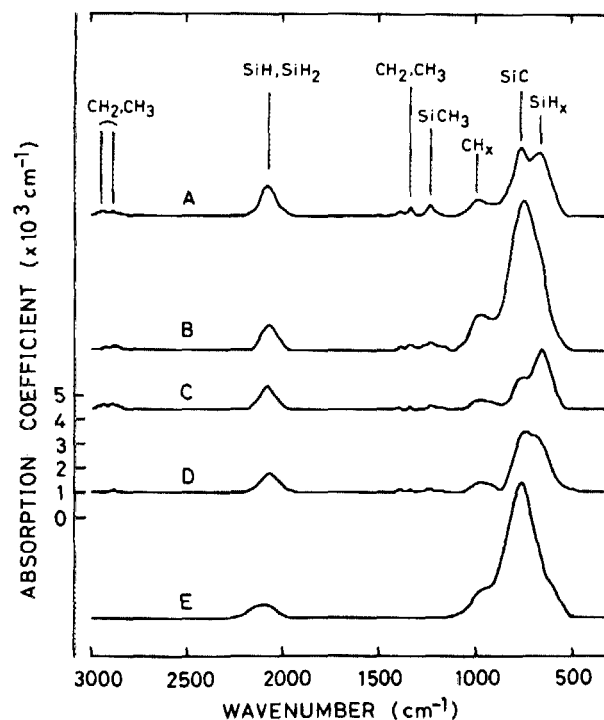


FIG. 3. Typical infrared absorption spectra of the films having 2.0 eV optical gap (E_0) deposited from (A) CH_4/SiH_4 (diode), (B) CH_4/SiH_4 (triode), (C) $\text{C}_2\text{H}_4/\text{SiH}_4$, (D) $\text{SiH}_3\text{CH}_3/(\text{SiH}_3\text{CH}_3 + \text{SiH}_4)$, and (E) $\text{H}_2/(0.8\text{CH}_4 + 0.2\text{SiH}_4)$ plasmas, respectively.

the carbon alloys, possibly due to the strong surface reaction of carbon-related radicals.

Figure 3 shows the infrared absorption spectra of the films having optical gaps close to 2.0 eV for the following preparation conditions: (A) CH₄/SiH₄, (B) triode CH₄/SiH₄, (C) C₂H₄/SiH₄, (D) SiH₃CH₃/SiH₄, and (E) H₂-dilution CH₄/SiH₄. It should be noted that the CH₂, CH₃, and SiCH₃ configuration modes are clearly observed in all of the films from A to D in addition to SiH_x stretching and rocking, CH_x rocking, and SiC stretching modes,⁵ while only SiH_x, CH_x (rocking), and SiC stretching modes are observed in the film E.

Phenomenologically, it is likely that the carbon polyhydride mode (CH₂, CH₃) configurations as well as the SiCH₃ mode configuration give rise to the deterioration of photoelectric properties of the films through the introduction of a low-density-network structure and a higher degree of disorder in the film.

Figure 4 shows the atomic density (N_H) of incorporated H in the film determined by the thermal evolution technique.⁶ As shown in the figure, a larger number of H atoms are incorporated in *a*-SiC:H films prepared from nondiluted plasmas compared to *a*-SiC:H ($E_0 \approx 2$ eV) from both the H₂-dilution plasma as well as *a*-Si:H ($E_0 = 1.7$ eV), although the absolute value of N_H might be overestimated because the densities of the *a*-SiC:H films prepared by the conventional methods are low, seen by the change in the refractive index shown in Fig. 2. This is consistent with the results of Fig. 3, because carbon polyhydrides as well as SiCH₃ configurations are introduced in the network structure of *a*-SiC:H prepared from conventional nondiluted methods, resulting in an increase in the atomic density of H. It is still an open question as to why the atomic density of H in *a*-SiC:H is drastically reduced when using the H₂-dilution plasma, although some speculative remarks are made as follows:

(1) Hydrogen atoms reaching the growing surface etch out weakly bonded radicals, resulting in a dense random network.

(2) Hydrogen atoms reaching the surface act as a "toupée for the partially bald surface" due to the following reaction: CH_x + H (surface) = CH_{x+1}. This leads to a decrease of the reactivity of the radicals at the growing surface. A detailed discussion of the role of H atoms on the growth process of *a*-SiC:H, resulting in a high-density-network structure, will be reported elsewhere.

In summary, the previously observed rapid degradation of electronic properties associated with the introduction of C to *a*-Si:H to form wider band-gap alloys can be attributed to the low-density-network structure of the film. This low density network also results in a large degree of H incorporation.

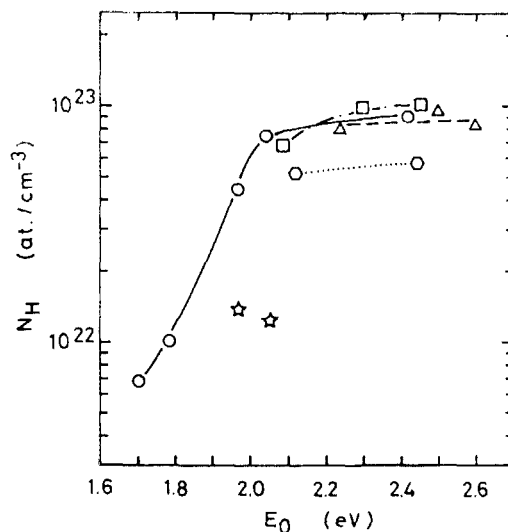


FIG. 4. Number of H atoms incorporated in *a*-SiC:H films determined by the thermal evolution method. (Symbols same as Fig. 1.)

However, by modulating the growing surface through H₂ dilution of the plasma, a highly photosensitive hydrogenated *a*-SiC:H alloy showing a photo-to-dark conductivity ratio of 10⁷ at a band gap of 2.0 eV was realized.

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