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Effect of Ion Bombardment on the Growth and Properties of Hydrogenated Amorphous Silicon-Germanium Alloys

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We report a systematic investigation of the effect of ion bombardment during the growth of amorphous silicon-germanium alloy films from silane and germane rf-glow discharge. Independent control of the plasma and the ion flux and energy is obtained by using a triode configuration. The ion contribution to the total deposition rate can reach 20% on negatively biased substrates. Although the Si and Ge composition of the film does not depend on the ion flux and energy, the optical, structural and electronic properties are drastically modified at low deposition temperatures when the maximum ion energy increases up to 50 eV, and remain constant above 50 eV. For a Ge atomic concentration of 37% and a temperature of 135°C, the optical gap decreases from 1.67 to 1.45 eV. This is correlated with a modification of hydrogen bonding configurations. Silicon dihydride sites disappear and preferential attachment of hydrogen to silicon is reduced in favour of germanium. Moreover the photoconductivity increases which shows that ion bombardment is a key parameter to optimize the quality of low band gap amorphous silicon-germanium alloys.

KEYWORDS: ion bombardment, film growth, a-SiGe, glow discharge

§1. Introduction

In plasma-enhanced chemical vapor deposition (CVD), in particular the deposition of hydrogenated amorphous silicon (a-Si:H) or Si based alloys, such as a-Si:Ge:H, from silane (SiH_4) or silane-germane (SiH_4–GeH_4) glow discharges, the effect of ion bombardment on the growth process and on the resulting material properties is still controversial. In which deposition conditions does the ion bombardment improve or deteriorate the structural and optoelectronic properties of these semiconducting films, in view of device applications? In other words, what is the optimal range of ion flux and ion energy needed to take advantage of the ion momentum transfer to the reactive species adsorbing on the growing film surface, while avoiding ion-induced damages by implantation? The answer to these questions is not obvious since the effect of ion bombardment is also related to the nature and surface reactivity of the neutral radicals contributing to the film growth, and it is difficult to vary, independently, the ion flux and energy and the plasma chemistry in a conventional rf-diode deposition system.

One strategy for obtaining the best device-quality a-Si:H or a-SiGe:H films consists of selecting the deposition conditions where the ion flux is negligible but the neutral radicals have a low sticking probability and a high surface mobility. The good candidates, among SiH_4 or GeH_4 fragments, are the SiH_3 and GeH_3 radicals which cannot insert directly into Si–H or Ge–H surface bonds on the growing film. For a-Si:H deposition, these conditions are usually obtained in low power (typically 10 mW/cm^2 of the rf-electrode) and moderate pressure (50-100 mTorr) SiH_4 discharges.$^{1)}$ The role of the SiH_3 radical and the surface reaction mechanisms have been further elucidated by using the triode discharge configuration in order to separate SiH_3 from other radicals such as SiH_2, SiH, Si,$^{2)}$ or by using a nonplasma method, such as Hg-photosensitization of SiH_4, which is a selective source of SiH_3 radicals.$^{3,4)}$ Moreover, in the case of a-SiGe:H deposition, it has been demonstrated that the triode configuration leads to a noticeable improvement in film quality$^{5,6)}$ which is ascribed to the radical separation effect enhancing the SiH_3 and GeH_3 contribution to the film growth. For further improvement of the SiH_3 and GeH_3 surface mobility, it has also been shown that the hydrogen coverage of the film surface should be increased by hydrogen dilution of the starting gases, SiH_4 and GeH_4, in order to enhance the yield of atomic hydrogen on the surface.$^{7)}$

If high sticking probability and low surface mobility radicals such as SiH_2, SiH or Si are involved, so that the film structural, optical and electronic properties tend to be deteriorated, ion bombardment at a moderate energy (typically 50 eV) can induce a drastic change in the film growth process, which favors a densification of the material and a modification of the hydrogen incorporation and bonding modes. This has been clearly demonstrated in very low pressure (0.5–4 mTorr) dc-multipole SiH_4 discharges by varying the ion energy between 5 and 150 eV without modification of the plasma.$^{8-12)}$ It has also been reported that a-Si:H film properties are significantly improved by ion bombardment in a dc-discharge at much higher pressure (0.22 Torr) when the substrate is located in the positive column region and negatively biased by the application of an rf voltage.$^{13)}$ Similar improvements upon biasing the substrate electrode are observed in rf-discharges at low SiH_4 partial pressures (typically 5-10 mTorr),$^{14)}$ or when SiH_4 is diluted in hydrogen$^{15)}$ or in a rare gas,$^{16)}$ i.e., when the contribution of the SiH_3 radical is probably not domi-

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*Permanent address; Laboratoire de Physique des Interfaces et des Couches Minces (E. R. du CNRS), Ecole Polylechnique. 91128-PALAISEAU Cedex, FRANCE nant; moreover, the influence of the nature of the diluent rare gas has also been ascribed to ion bombardment effects.[17] Recently, a comparative study of the growth processes of a-Si:H and a-Ge:H films by spectroscopic ellipsometry has shown similar reductions in the film roughness and improvement in the film density upon application of a dc negative bias on the substrate electrode,[18] which suggests that the quality of a-SiGe:H films could also be improved by this method.

In this paper we report a systematic study of the effect of ion bombardment on a-SiGe:H film growth kinetics and properties. The ion flux and energy are varied without changing the plasma chemistry, hence the nature of neutral radicals and ions contributing to the film growth is investigated by using the triode discharge configuration. The film properties are analyzed by a combination of optical, electrical and chemical characterizations.

§2. Experimental

The triode discharge system has been presented elsewhere.[2] In this study, the distance between the rf-powered electrode (13.56 MHz) and the mesh electrode was 4 cm. The diameter of the rf-electrode was 10 cm. In order to prevent lateral spreading of the plasma, the mesh electrode was dc-biased at 40 V. The substrate electrode was positioned at 0.5 cm from the mesh. At this small distance, the radical separation is not yet achieved, so that the high sticking probability and low mobility radicals contribute significantly to the film growth.[2,7] Using pure SiH_4 and GeH_4 (no H_2 dilution) at a total pressure of 25 mTorr and gas flow rates of 4 sccm and 0.5 sccm, respectively, a-Si:Ge:H films, with a Ge atomic concentration of 35–40%, were deposited at two substrate temperatures, $T_s = 135°C$ and 295°C. The rf power actually coupled to the plasma was 20 Watts, i.e., about 0.25 W/cm^2 at the rf-electrode.

A variable dc bias (V_B) was applied to the substrate electrode from -110 to $+65$ V with respect to ground. The ion flux and ion energy on the substrate electrode were measured using a double-grid electrostatic energy analyzer.[8,14,18] The ion flux (ϕ_+) was obtained from the measured ion current, normalized to the grid transparency and to the analyzer area. From the measured film deposition rate, converted into a total flux (ϕ_0) of depositing Si and Ge atoms by assuming a film density of 5×10^{22} atoms/cm^3, as for crystalline silicon c-Si, the ion contribution to film growth (ϕ_+/ϕ_0) was derived. The fraction of H^+, H_2^+ and H_3^+ ions remains negligible as compared to SiH_m^+ and GeH_m^+ ions.

The substrate used for the material characterization had to possess sufficient conductivity in order to maintain the surface electrical potential. We used c-Si and glass covered with SnO_2 as a transparent conducting oxide (TCO). The film thicknesses were measured by the stylus method. The real refractive index (n) at a wavelength of about 1.5 μm was obtained from the interference fringes in the near-IR transmission spectra of samples on TCO. From the UV-visible absorption coefficient (α) as a function of photon energy ($h\nu$), two values of the optical gap were determined: E_{0T} was obtained by the Tauc method from a linear extrapolation of $(\alpha h\nu)^{1/2}$ according to the relation

$$(\alpha h\nu)^{1/2} = B(h\nu - E_{0T}) \tag{1}$$

and E_{04} is the photon energy at which $\alpha = 10^4$ cm^{-1}. The Ge concentration in the film was measured by Auger electron spectroscopy. Raman spectra were also measured in an attempt to detect any change in the distribution of Ge–Ge, Si–Ge and Si–Si bonds from the intensities and linewidths of TO and TA phonon modes.[19] The hydrogen incorporation and bonding modes were analyzed from IR absorption spectra and thermal evolution of H_2 at a heating rate of 20°C/min. The dark conductivity σ_d and the photoconductivity ($\Delta\sigma_p$) under standard AM1 illumination were measured in the sandwich configuration, between the TCO and an evaporated Mg electrode, which is known to give a good ohmic contact on a-Si:H.[20]

§3. Results and Discussion

3.1 *Ion flux and energy distribution*

The ion current-voltage characteristics measured by the electrostatic analyzer on the substrate electrode, for different substrate bias (V_B) with respect to ground, are shown in Fig. 1. When increasing the retardation voltage V_R (with respect to V_B) applied to the second grid of the analyzer, the incoming ions are selected as a function of their kinetic energy. Therefore, the derivative of the ion current (I_+) with respect to V_R gives the ion energy distribution function (IEDF). The IEDF corresponding to $V_B = -110$ V is shown in Fig. 2.

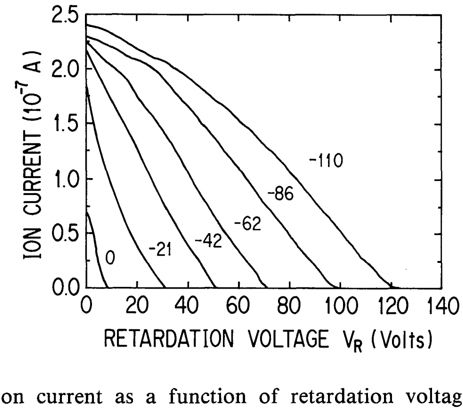


Fig. 1. Ion current as a function of retardation voltage (V_R) for different values of the substrate bias (V_B).

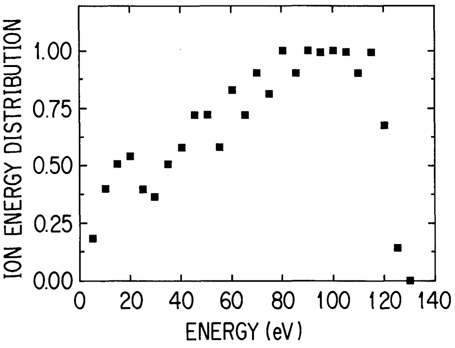


Fig. 2. Ion energy distribution function for $V_B = -110$ V as derived from the ion current characteristics shown in Fig. 1.

From Figs. 1 and 2 it can be seen that the maximum ion energy is approximately 10 eV larger than the value of e$|V_B|$. By assuming that this maximum energy corresponds to the free-fall kinetic energy of ions drifting between the plasma sheath boundary and the substrate, one derives that the average plasma is typically 10 eV with respect to ground, or equivalently 50 eV with respect to the mesh electrode biased at -40 V. However, various causes of broadening affect the IEDF.

First, the observed IEDF is the convolution of the true IEDF and the apparatus function which depends of the grid mesh size and spacing of the analyzer. However, from previous studies using this type of analyzer, we estimate this cause of broadening to be negligible. Secondly, the rf-modulation of the sheath induces a characteristic broadening,[21)]

$$\Delta W = C_0 (M_p/M_i)^{1/2} V_s^{3/2}/d, \qquad (2)$$

where M_p and M_i are the proton and ion mass, respectively, V_s is the average sheath potential drop, d the sheath thickness, and C_0 a constant inversely proportional to the rf frequency, which was found to be equal to 5.4×10^{-4} in eV·m/V$^{3/2}$ for 13.56 MHz discharges.[21)] In the present experiment, we consider that d and V_s refer to the sheath between the plasma and the mesh electrode since the substrate bias does not influence the discharge. Taking $V_s=50$ V, we assume that d is given by the Child-Langmuir expression,

$$d = (2e/M_i)^{1/4} (4\varepsilon_0/9J_+)^{1/2} V_s^{3/4}, \qquad (3)$$

where the ion current density on the mesh, $J_+ = 1.1\times10^{-5}$ A/cm^2, is deduced from the measured current at $V_R=0$ for $V_B=-110$ V, divided by the grid analyzer transparency and area, as well as by the mesh electrode transparency. We derive from eq. (3) that d is typically 1 cm, and from eq. (2) that ΔW can be as large as 14 eV for H$^+$, but is only 6 eV for SiH$_m^+$ ions ($M_i=30$ a.m.u.) and 4.9 eV for GeH$_m^+$ ions ($M_i=74$ a.m.u.). Such a broadening is still insufficient to explain the observed IEDF. Finally, the dominant causes of broadening are the ion-molecule collisions during the drift from the plasma-sheath boundary and the substrate electrode over a distance $d'=d+0.5$ cm. Indeed it has been shown elsewhere,[22)] that the transition from the Child-Langmuir to the mobility-limited theory for the sheath thickness[23)] occurs at such a small pressure in the case of SiH$_m^+$ ions in SiH$_4$ rf-discharges.

From Fig. 1 one can notice that the effect of increasing V_B from -110 V up to 0 V on the measured ion current at $V_R=0$ is similar to the effect of increasing V_R for $V_B=-110$ V. This demonstrates that the plasma is not perturbed by the substrate bias. However, the ion flux and ion energy cannot be varied independently due to the low energy tailing of the IEDF.

3.2 *Film growth rate*

The variation in the film growth rate (r_d) as a function of V_B is represented in Fig. 3 for the series of films deposited at $T_s=135$°C. r_d remains constant for a positive substrate bias down to 0 V, then increases rapidly with the ion current to the substrate between $V_B=0$ and -42 V (see Fig. 1), and saturates for $V_B<-42$ V when the ion current also reaches saturation. The same phenomenon is observed at $T_s=295$°C. Therefore, the relative increase of r_d can be attributed to the ion contribution to film growth. In Fig. 4 the values of r_d converted into atom flux (ϕ_0) are plotted as a function of the measured values of ion current converted into ion flux (ϕ_+). A linear increase of ϕ_0 is observed and the slope is nearly unity which suggests that the ion sticking probability is close to 1 (actually, the experimental value of the slope is 1.3 which would mean that ion bombardment also enhances the sticking probability of the neutral radicals). At the maximum ion current, ϕ_+/ϕ_0 reaches 20%. This value is quite large when compared to previously reported values in SiH$_4$ rf-discharges,[14,18,22)] but in the present case, both the low pressure and the high power density favor an increase in the ion flux and ϕ_+/ϕ_0. From the value of J_+ and the Bohm criterion relationship,

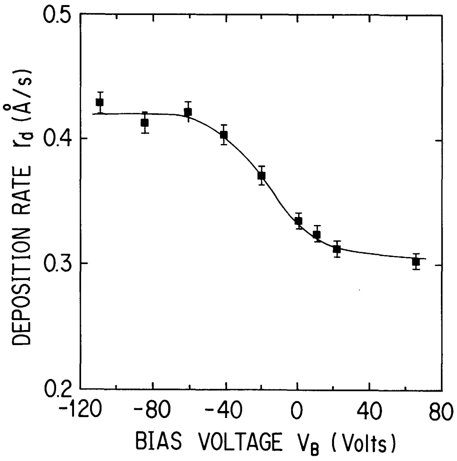


Fig. 3. Deposition rate (r_d) at $T_s=135$°C as a function of substrate bias (V_B).

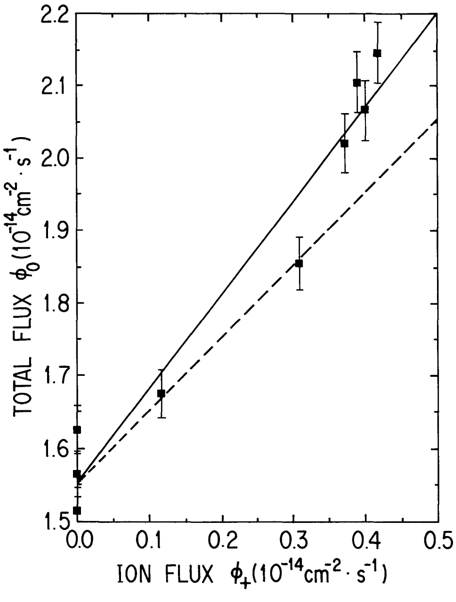


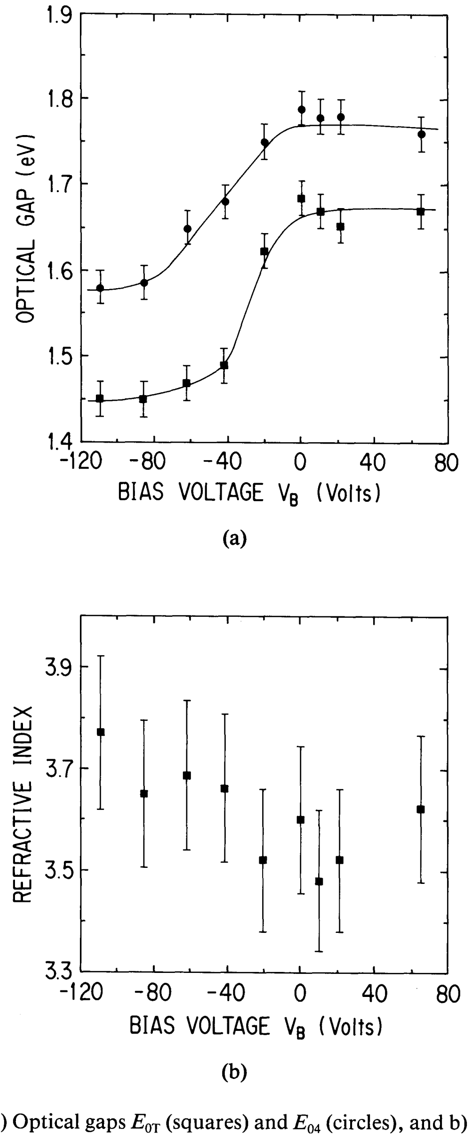
Fig. 4. Total flux (ϕ_0) of Si and Ge atoms contributing to film growth versus ion flux (ϕ_+). The solid line is a least square fit having a slope of 1.3, whereas the dashed line has a slope of unity.

$$J_+ = 0.5\ \mathrm{e}\, n_e (\mathrm{kT_e}/M_i)^{1/2}, \qquad (4)$$

the electron density (n_e) in the plasma is estimated to be about 8×10^8 cm^{-3}, assuming that the electron temperature is about 1 eV.

3.3 *Material properties*

The effect of ion bombardment was systematically studied on films deposited at low temperature, $T_s = 135$°C, where the structural and optoelectronic properties are much more affected than at high temperature. As shown in Fig. 5(a), both values of the optical gap, E_{0T} and E_{04}, for films deposited at $T_s = 135$°C, decrease by about 0.2 eV as the substrate bias is varied from 0 to about -50 V, i.e., when both the ion flux and energy increase. However, for $V_B < -50$ V, the optical properties are no more sensitive to a further increase in the ion energy at least up to 120 eV (the maximum energy of the $V_B = -110$ V condition, as shown in Fig. 2). In comparison, at $T_s = 295$°C, E_{0T} decreases only by 0.05 eV from 1.47 eV at $V_B = +65$ V down to 1.42 eV for $V_B = -110$ V. The slope B in the Tauc method of determination of the optical gap (see eq. (1)) remains constant around 800 (cm·eV)$^{-1/2}$ within the experimental precision. This indicates that the decrease of the optical gap induced by the ion bombardment is not due to a structural damage and disorder, which is usually correlated with a decrease in B.[24] As shown in Fig. 5(b), the refractive index (n) seems to increase slightly as the optical gap decreases. Again, this excludes structural damage with, for example, the presence of voids which would decrease n.



(a)

(b)

Fig. 5. a) Optical gaps E_{0T} (squares) and E_{04} (circles), and b) refractive index (n) as a function of substrate bias (V_B), for films deposited at $T_s = 135$°C.

A decrease in the optical gap and an increase in n would be expected if the Ge concentration in the film increases. However, no change of the chemical composition could be detected by Auger electron spectroscopy, the Ge atomic concentration [Ge]/{[Si]+[Ge]} in the film being remarkably constant at 37±3%, irrespective of the substrate bias or temperature. Further, since Raman spectra peak intensities and linewidths did not exhibit any significant change, it could also be concluded that the statistical distribution of Ge–Ge, Ge–Si, and Si–Si bonds are essentially conserved, and that ion bombardment does not induce a drastic structural disorder or, inversely, a preferential ordering in the Si–Ge network.

On the contrary, the H content and the H bonding modes to Si and Ge are strongly affected by ion bombardment. In the IR absorption spectra presented in Fig. 6, the 2100 cm^{-1} component of the stretching mode and the 840–890 cm^{-1} bending modes disappear for negatively biased samples, which reveals that ion bombardment reduces the dihydride, $=SiH_2$, and polymeric-like $(SiH_2)_n$ bonding configurations. Moreover, the median wavenumber of the wagging mode is slightly shifted from 630 cm^{-1} for $V_B = 20$ V to 614 cm^{-1} for $V_B = -110$ V, which indicates that the preferential attachment of hydrogen to silicon is fairly relaxed in favor of germanium. This suggests that a strong "ion-mixing" process takes place at the surface due to lateral momentum transfer of impinging ions. The thermal evolution curves of hydrogen presented in Fig. 7 also show that ion bombardment during film growth eliminates the weakly bonded hydrogen, which is consistent with the disappearance of $=SiH_2$ and $(SiH_2)_n$ bonding configurations. The variation of the total hydrogen content, $C_H = [H]$

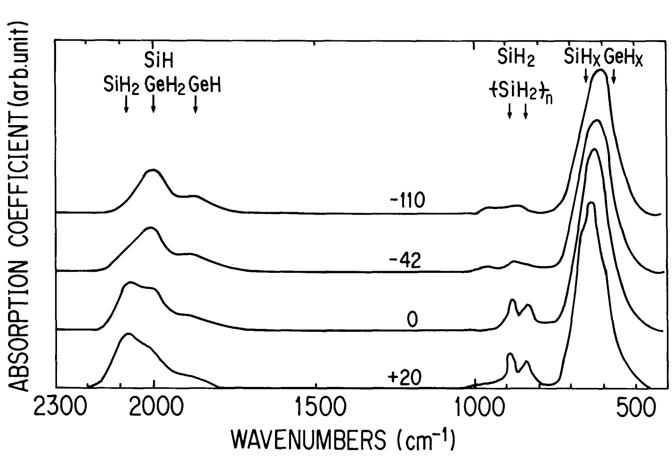


Fig. 6. Infrared absorption spectra of films deposited at $T_s = 135$°C for different substrate bias (V_B).

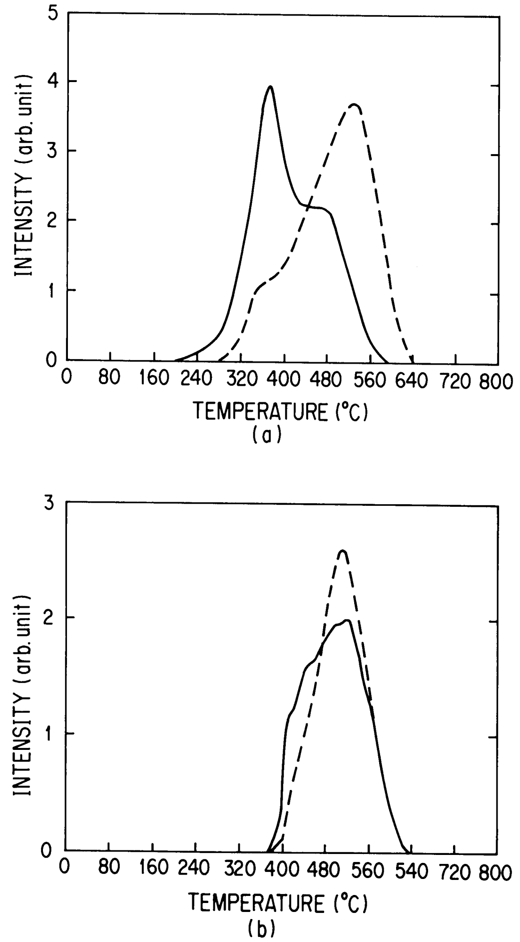


Fig. 7. Thermal evolution of hydrogen for a 20°C/mn, for films deposited at a) $T_s=135$°C and b) $T_s=295$°C, without ion bombardment (solid line) and with ion bombardment (dashed line).

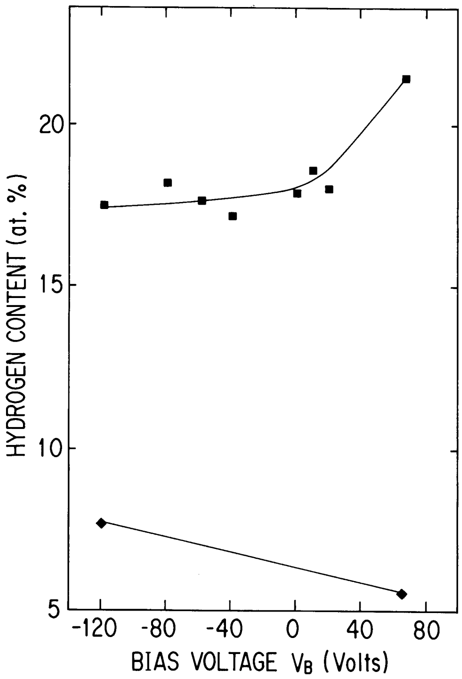


Fig. 8. Hydrogen content (C_H), as measured from thermal evolution of hydrogen for films deposited at $T_s=135$°C (squares) and $T_s=295$°C (lozenges), as a function of substrate bias V_B.

/{[Si]+[Ge]+[H]}, as measured by integration of the hydrogen evolution curves, is shown in Fig. 8. The decrease of both C_H and the optical gap at $T_s=135$°C would suggest, in a first approximation, that the effect of ion bombardment is similar to an increase in the effective temperature of deposition due to the ion momentum transfer at the surface, but this explanation is contradicted by the results at $T_s=295$°C where C_H increases with ion bombardment. Moreover, many previous studies of the effect of ion bombardment on the growth of pure a-Si:H have shown that the effect of ion bombardment is not simply reducible to a local heating. In many respects, the structural modifications induced in a-Si:H are similar to those presently observed in a-Si:Ge:H. For example, the range of ion energy in which most of the structural effect takes place is typically 0–100 eV,[9,10] the $=SiH_2$ and $(SiH_2)_n$ bonding configurations are suppressed as revealed by IR spectra,[8,11,15] and the weakly bonded hydrogen revealed by thermal evolution curves is eliminated.[12] However, the total hydrogen content (measured by nuclear reaction) was always found to increase as a function of ion energy or substrate negative bias, not only in low pressure dc-multipole SiH_4 discharges,[10] but also in rf discharges.[17] This rules out a simple heating effect of ions.

Complementary studies on a-Si:H films grown under ion bombardment have shed some light on the structure and on the growth process. From proton NMR* it appears that the elimination of $=SiH_2$ and $(SiH_2)_n$ bonding configurations by ion bombardment does not mean that all monohydride $\equiv$Si–H groups are dispersed in the random network; isolated Si–H bonds amount only to 4–5% in atomic concentration, whereas the remaining part of C_H corresponds to clustered $\equiv$Si–H monohydrides. Real-time and spectroscopic ellipsometry[8,9,12,18] and kinetic studies of oxidation[11] have shown a reduction in the porosity of the film, consistent with the elimination of the weakly bonded phase consisting of $=SiH_2$ and $(SiH_2)_n$ configurations. This means that the clustered $\equiv$Si–H are located at the interstices of close-packed dense units leaving no apparent microstructure. As also shown by ellipsometry, the surface roughness is erased by the "scouring" or "shot-peening" effect of ions.[25] An alternative or complementary interpretation is that the lateral ion momentum transfer to adsorbed neutral radicals enhances their surface mobility and their diffusion length. This tends to overcome the "self-shadowing" effect[25] characteristic of low mobility and high sticking probability species, and is responsible for the development of the surface roughness, porosity and columnar morphology.

The room temperature values of σ_d and $\Delta\sigma_p$, for the series of low temperature samples, are plotted in Fig. 9 as a function of V_B. The increase in σ_d for negative bias is consistent with the narrowing of the gap, hence with a decrease in the activation energy, which has been confirmed by temperature-dependent measurements of σ_d on a few samples. However, the increase in $\Delta\sigma_p$ indicates an improvement of the $\eta\mu\tau$ product, where η is the overall

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*J. Perrin and J. Boyce: unpublished results

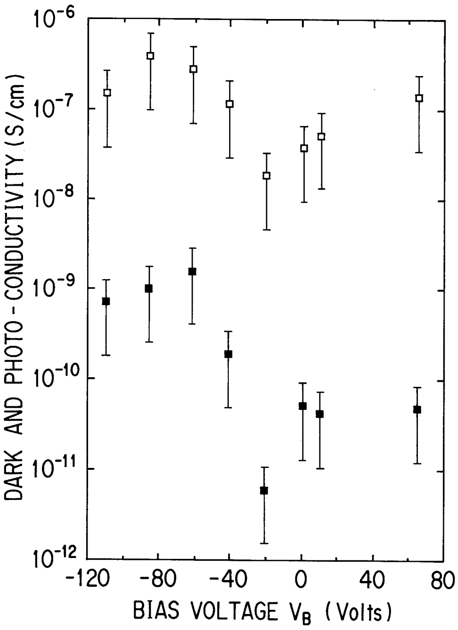

Fig. 9. Dark conductivity (σ_d) and photoconductivity ($\Delta\sigma_p$) as a function of substrate bias (V_B) for the series of films deposited at $T_s=135$°C.

quantum efficiency for electron-hole pair generation under AM1 illumination, and $\mu\tau$ the product of mobility and lifetime. η is not strongly affected by the decrease by 0.2 eV of the optical gap due to the broad wavelength range covered by the AM1 spectrum. Therefore the increase in $\Delta\sigma_p$ can be attributed to the improvement in $\mu\tau$. The increase in $\Delta\sigma_p$ with ion bombardment is also observed for the high temperature samples although to a lesser extent.

Since the search for highly photosensitive low-band gap amorphous silicon-germanium alloy is a primary goal to improve a-Si:H based photovoltaic solar cells, it is interesting to refer σ_d and $\Delta\sigma_p$ to the optical gap, and compare with other optimized a-SiGe:H alloys. In Fig. 10, we have plotted the present data as a function of E_{0T} and added a series a samples of variable Ge content deposited at $T_s=250$°C, either by the radical separation method, using the triode discharge at large substrate/mesh distance, or by the H_2 dilution method in diode discharge.[7] This series of samples have become a reference of typical best quality samples available today. It can be seen that the present samples deposited under controlled ion bombardment almost reach this limit. Keeping in mind that our photoconductivity measurement in the sandwich configuration are probably pessimistic, as compared to usual measurements in the planar configuration, it means that we have achieved a highly photosensitive low-band gap material at $T_s=295$°C and drastically improve at $T_s=135$°C the inferior material obtained without ion bombardment. Further studies of the electronic properties and especially the gap state density of states are in progress in order to elucidate the relation between optical, structural and electronic transport properties.

Another interesting issue is to understand why the optical gap strongly decreases at a constant Ge concentration as a consequence of the structural modification induced by ion bombardment. Nevertheless this phenomenon is not unique. We have verified that a reduction in the gap at a constant Ge concentration also occurs when applying the radical separation method to optimize the material obtained in the conventional diode configuration without H_2 dilution.[5]

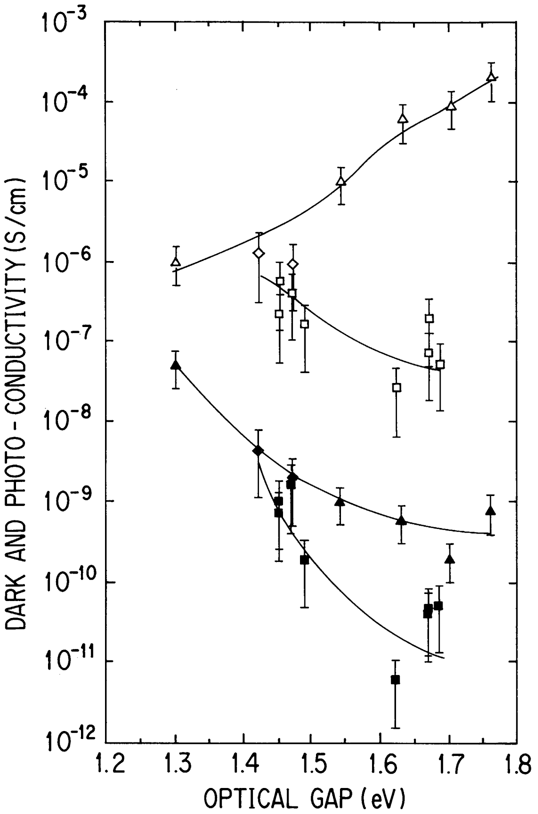

Fig. 10. Dark conductivity (σ_d) and photoconductivity ($\Delta\sigma_p$) as a function of optical gap (E_{0T}) for a-Si:Ge:H films deposited under variable ion bombardment at $T_s=135$°C (squares) and $T_s=295$°C (lozenges), and for a series of films of variable Ge content (triangles) deposited at $T_s=250$°C by the radical separation method in a rf-triode discharge except for the lowest gap (1.3 eV) sample which was obtained by the H_2 dilution method in a rf-diode discharge (see ref. 7).

§4. Conclusions

We have demonstrated that ion bombardment at moderate energy (≈ 50 eV), but reasonable current density ($\phi_+/\phi_0 \approx 20\%$), leads to a drastic improvement in the structural and optoelectronic properties of a-Si:Ge:H alloys, especially when the neutral species are not selected *a priori* for their low sticking probability and high surface mobility as in the radical separation method, and without hydrogen dilution to increase the surface hydrogen coverage. Although the detailed surface reaction mechanisms are much more complicated than in the case of pure SiH_3 and GeH_3 radical deposition, we attribute this improvement in the material properties essentially to the lateral ion momentum transfer which considerably enhances the surface mobility and diffusion in the first monolayer of adsorbed species, irrespective of their intrinsic chemical reactivity. This efficient ion-mixing, scouring or shot- peening effect eventually achieves the conditions of growth that can be attained otherwise by the soft methods using selected radicals or H_2 dilution. However, the radical separation or the H_2 dilution method both have the drawback of implying low deposition rate whereas such a limitation can be overcome in principle by the moderate-energy ion bombardment method. Indeed, this is our opinion that the excellent quality of the a-Si:Ge:H alloys obtained at a fast deposition rate (≈ 10 Å/s) using microwave excited plasmas, based on electron cyclotron resonance (ECR), at a very low pressure (1 mTorr),26) is precisely due to the high yield of the moderate energy electron in the plasma diffusion region. These ECR plasmas are very similar to the dc multipole discharge in which the effect of ion bombardment on the a-Si:H film growth has been previously demonstrated.8,9)

A second conclusion is that although various approaches have been used to improve the optoelectronic properties of a-SiGe:H alloys, there seems to be a saturation at the present time. This raises the fundamental question of whether we have reached the intrinsic limits of the material or it is still possible to go further by combining the different tools of the gas-phase and surface physicochemistry. Hopefully a better control of the ion bombardment, always present to some degree in conventional discharge, although largely ignored, will help to repel these limits.

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