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Amorphous Si and Si-based alloys from glow-discharge plasma

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Abstract - Growth process of a-Si:H films via the glow-discharge decomposition of SiH_4 is discussed by classifying the process into three categories; the radical generation process in the glow-discharge-SiH plasma, the radical transport process on the growing surface from the plasma and the growth-reaction process on the surface. The role of hydrogen atoms as well as ionic species is also mentioned. On the basis of the understanding of the film-growth kinetics from the plasma, drastic improvements of photoelectric properties of Si-based alloys are demonstrated.

INTRODUCTION

Hydrogenated amorphous silicon (a-Si:H) prepared via plasma CVD process has shown much promise as a material for thin film device applications such as solar cells, thin film transistors and photoreceptors (ref. 1-3). In order to control film properties for each application, the deposition kinetics of a-Si:H from so called non-equilibrium plasma has been desired to understand. For this purpose, a variety of plasma diagnostic techniques such as optical emission spectroscopy, mass spectrometry, diode laser absorption, laser induced fluorescence and coherent anti-Stokes Raman spectroscopy have been applied for the detection and the determination of the density of emissive, ionic and neutral radicals in the plasma. Radical separation technique has also been proposed to know the surface reaction process through a deposition behavior of selected and unified radical. This paper describes the film growth kinetics of a-Si:H from non-equilibrium SiH_4 plasma, and on the basis of the discussion for the a-Si:H deposition, the guiding principle for the improvement of photoelectric properties of Si-based alloy materials such as a-SiGe:H and a-SiC:H is driven.

GENERATION OF RADICALS IN THE SiH_4 PLASMA

Glow-discharge plasma is "Weakly-discharged plasma" in which the ion and electron density is low in the range between 10^8-$10^{10}/cm^3$, and the temperature of electrons is higher by two orders of magnitude than that of ions and neutral molecules. Figure 1 shows the energy distribution of electrons in the plasma calculated by Kushner (ref. 4) using the Monte-Carlo simulation as a function of the distance from the cathode, which suggests that the higher energy part is strongly modulated by the self dc-bias voltage automatically applied on the cathode.

Silane molecule (SiH_4) is excited to its higher energy state through an inelastic collision with energetic electrons in plasma, and is dissociated into a variety of neutral radicals, atoms, emissive radicals and ions. Figure 2 shows the dissociation, ionization and emission cross-sections as a function of electron energy for the electron impact on SiH_4 determined by Schmitt (ref. 5) using the multipole discharge device. Although the data in the figure suggest that the ionization and neutral dissociation are of comparable importance, the amount of ionic species and emissive species is expected to be much less than that of neutral radicals, because the average kinetic energy of electrons lies in the range between several eV at least in the bulk plasma as shown in Fig.1.

Actually, a relative number density of ionic species and neutral species was measured in the realistic plasma condition for a-Si:H deposition using mass spectrometry (ref. 6) under the ionizer-on and -off operations, and the number density of ionic species was estimated to be lower by three or four orders of magnitude than that of the neutral species. As for emissive species, Si* and SiH* emission intensity were measured and the number density of Si* and SiH* of excited states in the steady-state plasma was estimated to be 10^6-$10^7/cm^3$ using their optical transition probabilities. These values are also lower by five or six orders of magnitude than the density of species required for explaining the observed deposition rate of a-Si:H.

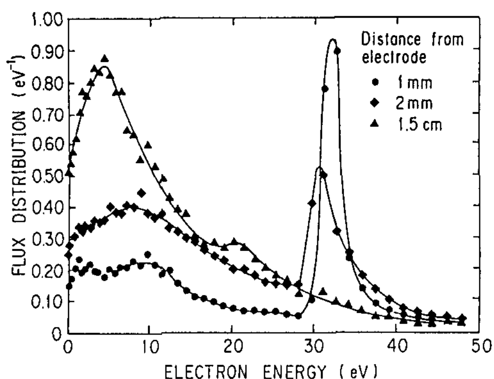

Fig.1. Energy distributions in the glow-discharge plasma (ref. 4).

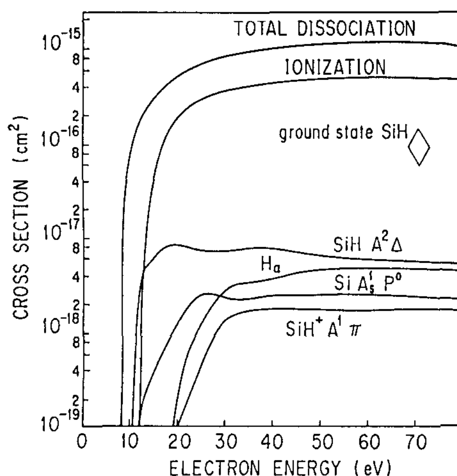

Fig.2. Cross sections for the electron impact process (ref. 5).

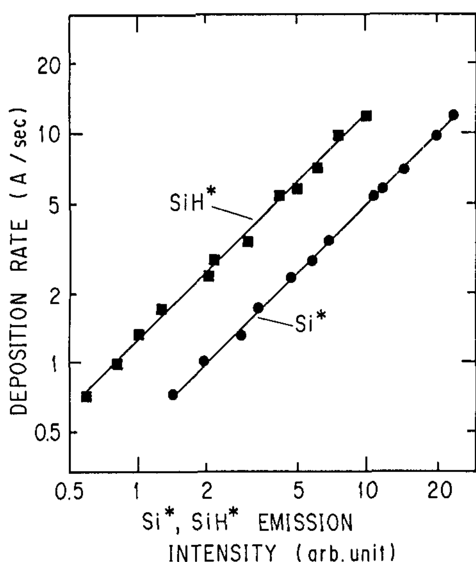

Fig.3. Relationship between the deposition rates and the emission intensities of Si* and SiH*.

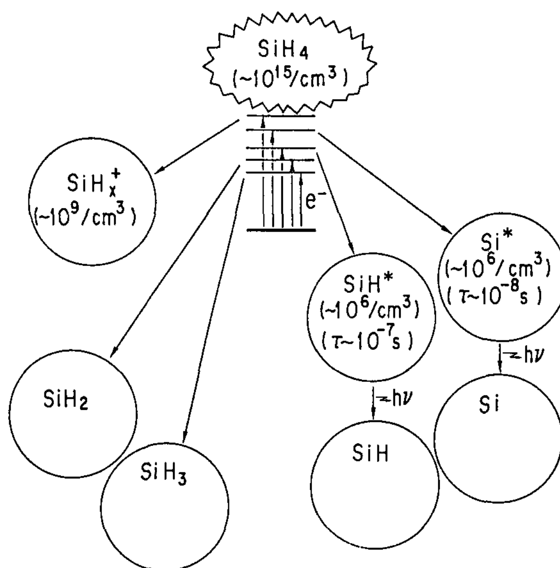

Fig.4. Schematic representation of electron-impact process and steady-state densities of ionic and emissive species.

However, a fine one-to-one correlation has been observed (ref. 7) between the emission intensity of either Si* or SiH* and the deposition rate of a-Si:H under various realistic plasma conditions when the SiH_4 pressure and substrate temperature are kept constant, as is shown in Fig.3. This proportionality suggests that the emission intensities of Si* and SiH* are proportional to the flux density of the film precursors (neutral SiHx) reaching the growing surface. It is well known that the emission of Si* as well as SiH* is produced through one electron-impact process to SiH_4 (ref. 8). Namely, the film precursors SiHx are also generated via one-electron impact process to SiH_4 in the plasma. Thus the primary radical-generation process in the plasma can be sketched as shown in Fig.4.

The number density of neutral Si and SiH radicals in their ground state were estimated by Schmitt et al. (ref. 9) and Matsumi et al. (ref. 10) using LIF, and Si as well as SiH is too low to explain the total deposition rate of a-Si:H from conventional deposition conditions. Consequently, it is speculated that the primary electron-impact process generates a variety of neutral, ionic and emissive radicals and atoms, and that the main precursors for the film deposition are likely to be neutral SiH_2 and SiH_3, while the direct contribution of ionic as well as emissive species can be neglected to the film deposition of a-Si:H in the conventional deposition condition.

RADICAL TRANSPORT ONTO THE GROWING SURFACE

Neutral radicals and ions generated in the plasma are transported onto the substrate surface through various secondary reactions mainly with parent SiH_4 molecules. The important reaction-rate constants for the secondary process taking place during the transport are listed in Table 1. In various radicals and atoms generated by the primary process, SiH_3 has a quite long reaction-lifetime, because SiH_3 reacts with parent SiH_4 forming SiH_4+SiH_3 again. On the other hand, SiH_2, which is likely one of the main products in the plasma, reacts with SiH_4 forming Si_2H_6 which has no reactivity on the growing surface.

Table 1. Important reaction and their reaction rate constants (cm^3/sec) for the radical transport process.

Reaction	Rate constant
$Si + SiH_4 \rightarrow Si_2H_4 \rightarrow Si_3H_8$	4×10^{-11}
$SiH + SiH_4 \rightarrow Si_2H_5 \rightarrow Si_2H_6 + SiH_3$	$> 3.3 \times 10^{-12}$
$SiH_2 + SiH_4 \rightarrow Si_2H_6$	1.1×10^{-10}
$SiH_3 + SiH_4 \rightarrow SiH_4 + SiH_3$	
$H + SiH_4 \rightarrow H_2 + SiH_3$	8.5×10^{-12}
$SiH_2 + H_2 \rightarrow SiH_4$	8×10^{-15}

Considering the branching ratio of radicals in the SiH_4 plasma as well as the lifetime of each radical during the transport to the growing surface, a fairy part of radicals reaching the surface are speculated to be SiH_3 in the realistic SiH_4 glow-discharge case, which has been experimentally confirmed by Longeway et al. (ref. 11) and Robertson et al. (ref. 12). However, it should be noticed that other radicals reaching the surface such as Si, SiH and SiH_2 also contribute to the film growth although their concentration seems to be quite lower than that of SiH_3. Those species affect the structural and photoelectric properties of the resulting films through different reaction modes on the growing surface when their fraction in the total flux density of the precursors becomes larger.

FILM GROWTH PROCESS ON THE SURFACE

Radicals and atoms reaching the growing surface are adsorbed on the surface. Part of them start diffusing on the surface and make chemical bonds at some site forming amorphous network structure, while others are desorbed depending on their sticking coefficient on the surface.

A network structure of a thin film is principally determined by the energy-relaxation process of adsorbed precursors. A defective material with a low-density network is likely to grow when the surface diffusion coefficient is too low for adsorbed radicals to find out their energetically favorable site. Therefore, for producing a dense network structure with a low defect density, surface diffusion coefficient should be large (ref. 13). The surface diffusion coefficient of adsorbed radicals is described as

$$Ds = \nu a_0^2 \exp(-Es/kT), \qquad (1)$$

where ν is the vibrational frequency of species, a_0 the jump distance and Es the activation energy for the site jumping.

In order to obtain a larger Ds of adsorbed radicals, the surface temperature should be raised. At lower temperatures of T_s<300C a growing surface is considered to be covered with hydrogen (H). According as T rises, removed process of surface-covered H takes place, and in T_s>350C the H-coverage factor starts to decrease. It results in the reduction in the surface Ds because the effective activation energy for the site jumping (Es) increases due to the higher reactivity of Si free bonds with adsorbed radicals. Thereby, there exists the optimum temperature for obtaining the dense network structure in the a-Si:H deposition process. Figure 5 shows the photo- and dark conductivities of the deposited films plotted against the substrate temperature during the growth. As shown in the figure, photoelectric properties of the resulting films are strongly dependent on their growth temperature and take the maximum value against the substrate temperature, which clearly indicates that Ds is the key factor for determining the properties of the resulting film through the change of film structure.

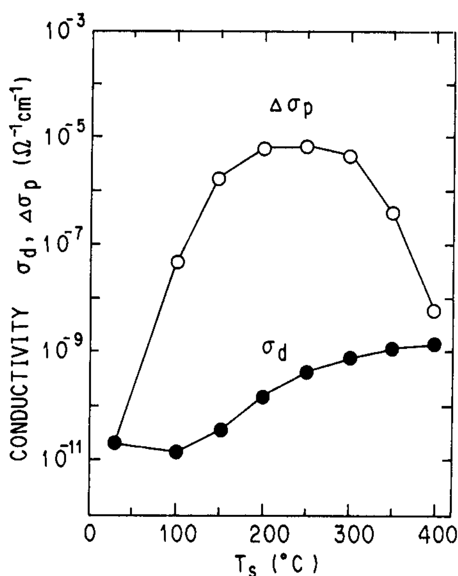

Fig.5. Photo- and dark conductivities of a-Si:H plotted against substrate temperature.

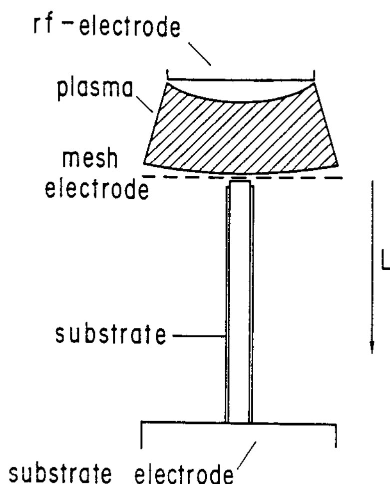

Fig.6. Triode configuration used for the radical separation technique.

In order to understand the reaction behavior of SiH_3 radicals on the growing surface, radicalseparation technique was used (ref. 14). As shown in Table 1, SiH_3 has a longer reacton lifetime in all SiHx and H in the plasma, which enables us to select SiH_3 using a triode configuration as shown in Fig.6. Figure 7 shows the deposition rate plotted against the square of the distance (L^2) between the mesh and substrate for various substrate temperatures. A drastic increase in the deposition rate from 300C to 460C is considered to originate from a change in the H-coverage factor. The deposition rate at 460C is thought to give directly a relative flux density of impinging SiH_3 to the growing surface at each L, because SiH_3 has a unity sticking coefficient on the H-deficient surface. Figure 8 shows the relationship between the deposition rate at 300C and that at 460C. As is seen in the figure, the deposition rate for the H-covered surface reveals a clear bend from a square-law

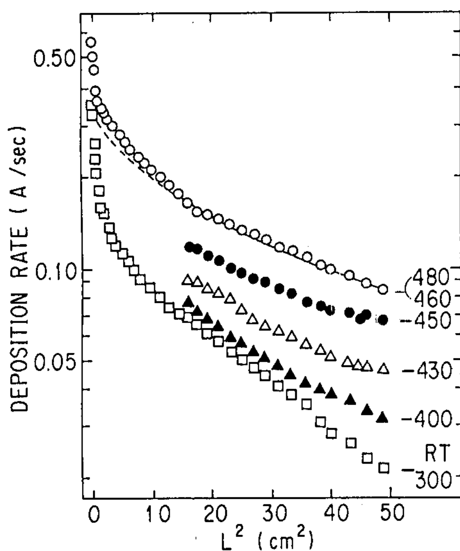

Fig.7. Deposition rate plotted against the square of the distance between the mesh and substrate for various substrate temperatures.

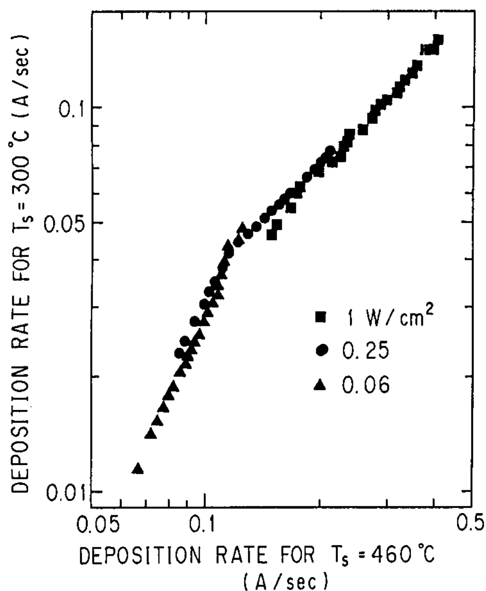

Fig.8. Deposition rate at 300C plotted against that at 460C.

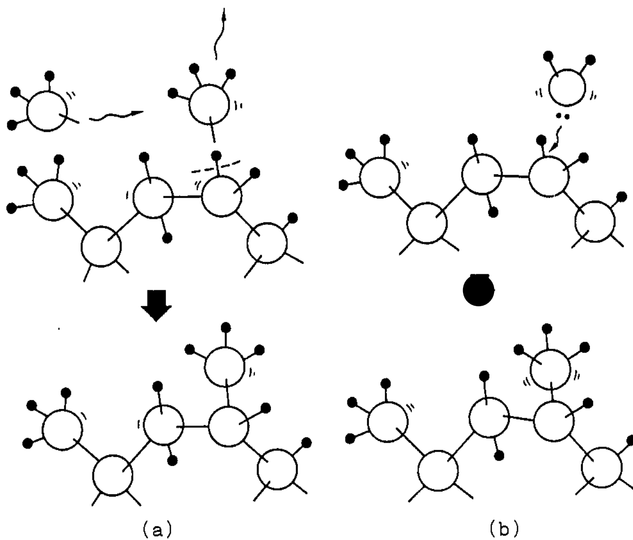

Fig.9. Surface-reaction models for (a) SiH_3 and (b) SiH_2 radicals.

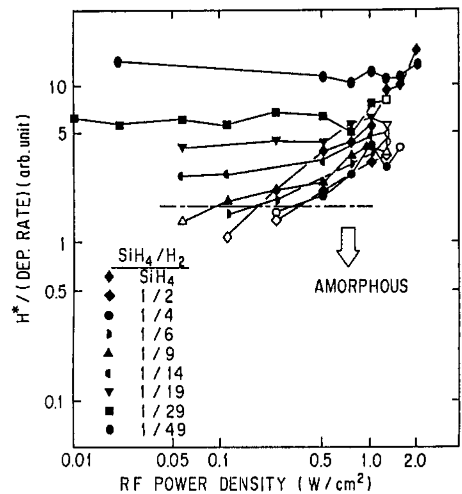

Fig.10. Ratio of H* emission intensity to the deposition rate vs. rf-power density.

regime to a linear-relation regime against the flux density of impinging SiH_3. On the H-covered surface, it is speculated that a SiH_3 radical contributes to the film deposition through a bimolecular reaction, as is shown in Fig.9(a). Namely, a SiH_3 can deposit on the surface only when the H is extracted by another SiH_3. In other words, a SiH_3 radical has a low sticking coefficient and larger Ds at least when the surface is covered with H.

On the other hand, other radicals such as Si, SiH and SiH_2 can easily stick to the surface even when the surface is covered with H through a insertion reaction, as is shown in Fig.9(b). Namely, Si, SiH and SiH_2 radicals have smaller Ds on the growing surface.

ROLE OF HYDROGEN ATOMS

The important role of hydrogen (H) atoms reaching the growing surface is to increase H-coverage factor on the growing surface and, thereby, to enhance the surface diffusion of radicals, which has been confirmed through the observation of the microcrystalline-amorphous mixed-phase Si:H (μc-Si:H) deposited from the glow-discharge plasma.
Figure 10 shows the ratio of H* emission intensity in the plasma to the film deposition rate, which is proportional to the number of hydrogen atoms reaching the surface during a monolayer-deposition time, as a function of the rf-power density at a constant substrate temperature (350C). Structure of deposited Si:H films becomes amorphous or microcrystalline depending on deposition conditions, and solid symbols represent the formation of μc-Si:H, while open symbols indicate amorphous structure. As shown in the figure, the lower limit of H*/(dep. rate) exists for the formation of μc-Si:H, suggesting that the sufficient H-coverage factor is required for the formation of μc-structure.

Figure 11 shows the volume fraction of microcrystallites in the film determined by the X-ray diffraction method plotted against the substrate temperature (Ts) during the deposition. Volume fraction of microcrystallites reveals a strong dependence on Ts, taking a maximum value at around 400C and tending to zero in lower as well as higher Ts ranges.

In the normal deposition condition of H*/(dep. rate) below the critical value in Fig.10, μc structure does not appear in the whole temperature range between room temperature and 500C. Only when H*/(dep. rate) exceeds the critical value, the volume fraction of microcrystallites shows a strong dependence on Ts. It suggests that the structure of resulting films is strongly affected by the H-coverage factor through the change in the surface diffusion coefficient of adsorbed radicals. Namely, when the growing surface is sufficiently covered with H, the reaching radicals such as SiH_3 have a larger surface diffusion coefficient and can find out an energetically stabler site to form a denser random network, as is discussed above, but, in an extreme case, they reach the stablest site, resulting in the formation of microcrystalline structure.

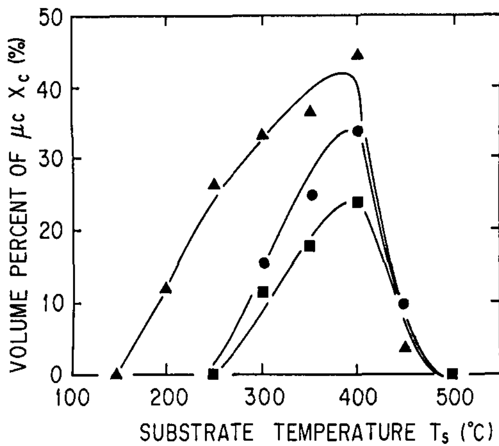

Fig.11. Volume fraction of micro-crystallites in the film vs. substrate temperature.

As another role of hydrogen atoms reaching the growing surface, etching effect of Si from the growing surface has been pointed out. However, it is clear from the one-to-one correspondence between the emission intensity of Si* or SiH* from the plasma and the film-deposition rate (see Fig.3) that the etching rate of Si by H might be negligibly small and does not affect the deposition rate of a-Si:H and μc-Si:H in the case of the conventional conditions.

ROLE OF IONIC SPECIES

Since the number density of impinging ions onto the growing surface is much lower than that of neutral radicals such as SiHx and H, the contribution of ionic species to a total deposition rate of the film can be neglected. However, ionic species are accelerated by an electric field between the bulk plasma and the substrate electrode, and get higher kinetic energies as compared with the neutral radicals, which causes a non-negligible effect on the film properties.

The role of ionic species was studied through the experiment of power-source frequency dependence on the properties of resulting films, whereby the number of impinging ions can be changed without changing the number as well as the sort of reaching radicals. Figure 12 shows the total amount of ionic species impinging onto the growing surface which were measured by mass spectrometer set below the substrate electrode, as a function of power-source frequency. Number of impinging ions involving H^+, H_2^+, $SiHx^+$ and Si_2Hy^+ drastically increases when the frequency decreases from 1MHz to 500kHz. This increase of ionic species is due to the reduction in dc self-bias voltage on the cathode caused by a decrease of the frequency. Namely, the ionic species are unable to follow the cycle of polarity change of the rf-electric field when the frequency exceeds a critical cut-off value expressed as

$$fc = e\lambda E/2\pi mvL, \qquad (2)$$

where λ, E, m, v and L are the mean free path of each ionic species, the magnitude of electric field, the weight of each ion, its thermal velocity and the electrode distance, respectively.

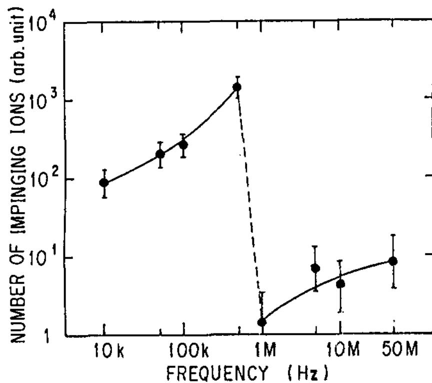

Fig.12. Amount of ionic species impinging onto the growing surface vs. power-source frequency.

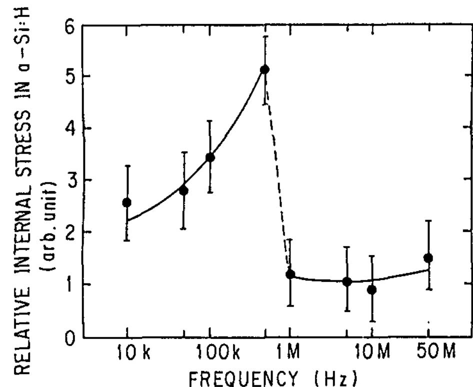

Fig.13. Relative internal compressive stress vs. power-source frequency.

Figure 13 shows the relationship between the relative internal compressive stress stored in the deposited film measured by the laser-beam reflection technique and power-source frequency used for the plasma generation. As is clearly shown in the figure, a relatively strong stress exists in the films which were deposited from SiH_4 plasma using an rf frequency lower than 500kHz, suggesting that the ionic species impinging onto the growing surface give rise to the internal compressive stress in a-Si:H. It should be noted that other film properties such as photo- and dark conductivity were not so strongly influenced by the increase of impinging ions on the growing surface.

IMPROVEMENT OF PHOTOELECTRIC PROPERTIES IN Si-BASED AMORPHOUS ALLOYS

Hydrogenated amorphous binary alloys such as hydrogenated amorphous Si-Ge and Si-C (a-SiGe:H and a-SiC:H) have attracted an increasing attention as key materials for the wide variety of applications, since the optical bandgap can be continuously controlled by changing their alloy compositional ratio. However, in contrast to a-Si:H, a-SiGe:H and a-SiC:H prepared from the conventional glow-discharge decomposition of SiH_4/GeH_4 and SiH_4/CH_4 mixture show the inferior photoelectric properties.

Key factors in the film growth process for the improvement of film quality are essentially the same as those discussed above. Namely, less reactive radicals of SiH_3 and GeH_3 should be guided to the film-growing surface using a triode reactor, and the starting gas mixture is diluted with H_2 in order to make the H-coverage factor larger in the case of a-SiGe:H deposition. Figure 14 shows the dark conductivity and the photoconductivity of a-SiGe:H films prepared by the conventional "diode", the "triode" and "H_2-dilution" techniques, plotted against their optical bandgap (ref. 15), which demonstrates the drastic improvement of photoelectric properties of deposited a-SiGe:H by using triode as well as H_2-dilution techniques instead of the conventional deposition method.

The similar improvement has been done for the preparation of a-SiC:H by using the H_2-dilution technique (ref. 16). Figure 15 shows the photo- and dark conductivities of a-SiC:H films deposited by the conventional diode, triode and H_2-dilution techniques. As shown in the figure, a-SiC:H films deposited using the H_2-dilution technique reveal excellent photoelectric properties (star symbols) as compared with those from conventional as well as triode methods (other symbols).

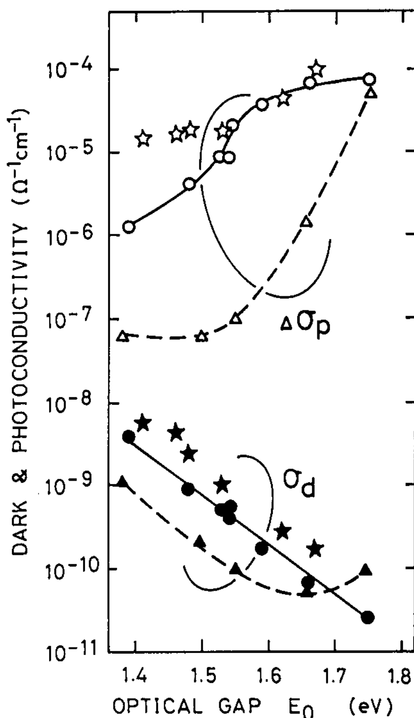

Fig.14. Dark and photoconductivities of a-SiGe:H; diode (triangles), triode (circles) and H_2-dilution (stars).

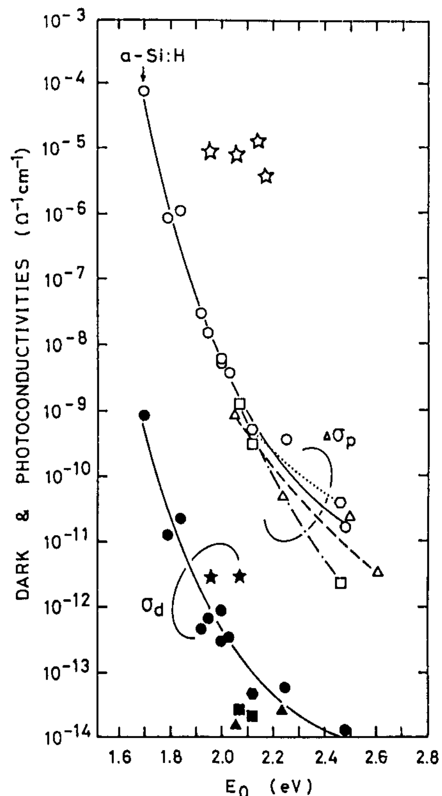

Fig.15. Dark and photoconductivities of a-SiC:H; H_2-dilution (stars), triode and diode (other symbols).

These remarkable achievements clearly indicate that the guiding principle for obtaining a high quality film in terms of "radical selection" and "high H-coverage factor of the growing surface" is valid not only in a-Si:H but also in alloy materials such as a-SiGe:H and a-SiC:H.

CONCLUSION

Growth process of a-Si:H films via the glow-discharge decomposition of SiH_4 has been discussed by classifying the process into three categories: (1) radical generation process in the plasma, (2) radical transport process and (3) surface reaction process of reaching radical. On the basis of the understanding of the growth kinetics, the guiding principle has been presented for obtaining high-quality amorphous materials having a high-density network structure: (1) selection of less reactive radicals reaching the growing surface and (2) higher H-coverage factor of the growing surface, whereby a larger surface-diffusion coefficient of adsorbed radicals can be realized. This guiding principle has been applied to the preparation of Si-based alloys, and big improvements of photoelectric properties of these materials have been achieved.

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