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Densification of amorphous silicon prepared by hydrogen-ion-beam-assisted evaporation

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Hydrogenated amorphous silicon films were deposited by ion-beam-assisted evaporation onto substrates maintained at 120 °C. The influence of the substrate bias was studied. By combined infrared spectrometry and thermal desorption spectrometry experiments, it is inferred that the bombardment of the growing *a*-Si:H film by energetic hydrogen ions produces a densification of the material without modification of the Si:H bonding. © 1996 American Institute of Physics. [S0003-6951(96)01737-8]

It is well known that, by passivating the dangling bonds of silicon, hydrogen reduces the density of electronic states in the gap of amorphous silicon and renders the material suitable to electronic applications. Except the elaboration methods based on glow-discharge cracking of silane and sputtering in an Ar-H₂ atmosphere, several attempts have been made to introduce hydrogen into evaporated *a*-Si films. Since molecular hydrogen is relatively stable, appreciable Si-H bonding required the production of atomic hydrogen by dissociation of molecules in a heated tungsten tube¹ or the use of an ion beam from a Kaufman-type source.^{2,3} With ion-beam-assisted evaporation, ion bombardment is essentially independent of silicon deposition and both can be more easily controlled. Decoupling these processes can also bring useful information for the understanding of the *a*-Si:H deposition mechanisms.

The purpose of this study is to describe the growth of *a*-Si:H thin films using the electron cyclotron resonance (ECR) microwave plasma assisted evaporation method. The ECR microwave plasma sources are well known to provide high ion densities at low energies (10–25 eV). The pressures ($>10^{-5}$ Torr) required for stable operation of the source are compatible with the use of an electron beam gun. The reactive gas was pure hydrogen. The energy of the ions was varied by biasing the substrate. This letter shows that the accelerated hydrogen ions modify the microstructure of amorphous silicon. The films have been characterized by infrared spectrometry and thermal desorption spectrometry experiments.

The plasma generation chamber and the growth chamber were evacuated by a cryogenerator with a pumping rate of 1000 l/s. The background pressure was 10^{-8} Torr. Silicon was evaporated from an electron beam gun. The deposition rate (1 Å/s) was monitored and controlled by a quartz microbalance system. The samples were deposited on (111) Si substrates. Their thickness was 2400 Å. The hydrogen flow in the ion source was regulated by maintaining the total pressure P_{H_2} in the evaporation chamber at 4×10^{-5} Torr. The

2.45 GHz microwave energy of the ECR source was 200 W. A 875 G axial magnetic field was used to create electron cyclotron resonance and to promote efficient coupling of the microwaves to the plasma. The distance between the source and the substrate was 15 cm. The substrate temperature was regulated and maintained at 120 °C.

Samples were prepared with different substrate voltages equal to 0, –200, and –300 V. The hydrogen bonding configurations were obtained from Fourier transform infrared transmission measurements. Infrared spectra were recorded using a Perkin Elmer 2000 spectrometer with a resolution of 4 cm^{–1}. The contribution of an uncoated reference silicon substrate was subtracted from the experimental spectra. The type of hydrogen bonding was also studied by thermal desorption spectrometry experiments. The films were inserted into a quartz tube evacuated by an ionic pump and were heated at a constant rate of 10 °C/min to 800 °C. The base pressure of the chamber was 2×10^{-8} Torr. The gaseous components desorbing from the sample surface were detected by a quadrupole mass analyzer.

Infrared spectrometry spectra of samples prepared with substrate voltages equal to 0, –200, and –300 V are represented in Fig. 1 for the 1850–2300 cm^{–1} range and in Fig. 2 for the 500–1300 cm^{–1} range. For silicon prepared without bias, the Si-H stretching vibration modes are dominated by the band at 2090 cm^{–1}, which could be attributed to polyhydride groups SiH₂, (SiH₂)_n, and SiH₃ or to monohydride groups SiH located at internal surfaces or microvoids. A shoulder is clearly visible on the low-wave-number side: this band at 2000 cm^{–1} is associated to isolated SiH groups. Moreover, small bands appear at 2180 and 2240 cm^{–1}, which can be attributed to SiH or SiH₂ configurations containing oxygen atoms in their back bonds. For the same sample, two bands at 850 and 890 cm^{–1} are well visible. They correspond to the bending bands of polyhydride configurations and then confirm the important proportion of (SiH₂)_n or SiH₃ groups. Moreover, absorption bands at 1050 and 980 cm^{–1} indicate oxygen contamination, which appears when the samples are exposed to ambient air. The absorption band near 640 cm^{–1} is assigned to the wagging band of

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FIG. 1. Infrared absorption spectra in the range 1850–2300 cm^{-1} of $a\text{-Si:H}$ samples prepared with different hydrogen-ion energies. The indicated voltages U correspond to the substrate bias.

SiH_n ($n=1,2,3$). The bonded hydrogen content C_H was estimated from the integrated intensity of this band. With the usual proportionality constant $1.6 \times 10^{19} \text{ cm}^{-2,4}$ and an atomic density of silicon fixed to $5 \times 10^{22} \text{ cm}^{-3}$, C_H was estimated to be equal to 21%.

When the substrate is biased, the stretching vibration band is not modified. The oxygen-related bands have disappeared, but the proportion between the two peaks at 2000 and 2100 cm^{-1} remains unchanged. In the 500–1300 cm^{-1} range, the most striking difference is due to the disappearance of the oxidation peaks at 980 and 1050 cm^{-1} . The two bands at 850 and 890 cm^{-1} are always visible. They correspond to polyhydride bonds and are correlated to the 2100 cm^{-1} peak that remains in the stretching vibration band. The bias does not influence the hydrogen bonding. The hydrogen content deduced from the 640 cm^{-1} peak is equal to 27% and 26% for $U = -200 \text{ V}$ and $U = -300 \text{ V}$, respectively.

FIG. 2. Infrared absorption spectra in the range 500–1300 cm^{-1} of the samples described in Fig. 1.

FIG. 3. Thermal effusion spectra of the $a\text{-Si:H}$ samples described in Fig. 1.

Therefore, the evolution of the infrared spectra with the substrate bias is very different from that obtained with the substrate temperature since the hydrogen content decreases and the ratio of the bonds numbers SiH/SiH_2 increases with increasing temperatures.

The hydrogen effusion spectra of the three samples are represented in Fig. 3. The spectrum of the sample prepared without bias shows a peak around 400 °C. It strongly differs from the spectra obtained with glow-discharged silicon that present a desorption peak at 400 °C and a diffusion peak at 600 °C or only the high-temperature peak.⁵ But it is very similar to the spectra obtained for hydrogenated silicon prepared by sputtering⁶ or by evaporation⁷ on substrates maintained at 77 K. This peak is usually associated with desorption from internal surfaces in a void-rich material. In fact, there is also a slight shoulder on the high-temperature side. The principal peak corresponds to the SiH_2 units that are the dominant configurations, as shown by infrared spectrometry. The shoulder corresponds to the isolated SiH configurations. For $U = -200 \text{ V}$ and $U = -300 \text{ V}$, two other peaks appear at 260 °C and 550 °C. Their intensity increases with bias. The origin of the low-temperature peak is undetermined. The high-temperature peak could correspond to a diffusion phenomenon. An easy way to verify this hypothesis is the measurement of the thickness dependence. If diffusion limits the evolution rate, the rising diffusion length with increasing film thickness will result in a shift of the evolution peak to higher temperatures. Such a shift is really observed since the temperature of this peak increases from 480 °C to 580 °C when the thickness increases from 500 to 5000 Å. The first peak at 400 °C does not shift. By biasing the substrate, it is then possible to change the microstructure of the film because it presents no more postoxidation and some hydrogen atoms must diffuse through the film before desorbing. This microstructure change most likely corresponds to a densification of the material. Such a conclusion was already given for sputtered films that present low-density regions. It is generally admitted for these samples that dense microstructure is more resistant to postdeposition oxidation.⁸

The diffusion peak of the hydrogen-effusion spectrum

clearly appears for a voltage equal to 300 V. In order to confirm this threshold value, deuterated samples were prepared with different substrate voltages. For $U=0$ V and $U=-100$ V, the effusion spectra show only the desorption peak at 400 °C. For $U=-200$ V, the effusion spectrum was comparable to that of the hydrogenated sample prepared with $U=-300$ V. The microstructure change of the material is, therefore, dependent on both the bias and the ion mass. The models describing the mechanisms of the surface reactions in the deposition process of *a*-Si:H or *a*-C:H films by glow discharge^{9,10} cannot be applied because their surface is bombarded by hydrogen atoms and by SiH₃ or CH₃ radicals formed in the plasma. In the case of evaporation, the sticking coefficient of the evaporated silicon atoms is supposed to be equal to unity and the incident particles are the hydrogen molecules, atoms, or ions. A very simple model consists in saying that some incident hydrogen particles bond to silicon. Some hydrogen ions can also transfer their energy to the silicon atoms, which will improve their surface diffusion and then the densification of the microstructure. By considering a direct elastic collision between an incident hydrogen (deuterium) ion of mass m_1 and of energy $E_1=e|U|$ and a motionless silicon atom of mass m_2 , the energy of the silicon atom after the collision is $E_2=[4m_1m_2/(m_1+m_2)^2]e|U|$. The value E_2 has approximately the same value for hydrogen atoms with $U=-300$ V and deuterium atoms with $U=-200$ V. This simple model explains the ballistic effect of the hydrogen ions and shows that the diffusion peak appears

for an energy given to the silicon atoms approximately equal to 0.4 eV. This value could correspond to the activation energy of the surface diffusion of the silicon adatoms.

In summary, these ion-beam-assisted deposition experiments show that even bombardment by light ions accelerated with a moderate voltage can strongly modify the film structure. For hydrogenated amorphous silicon, hydrogen ions with 300 eV energy change neither the hydrogen content nor the proportion of SiH₂ and SiH bonds, but the postoxidation is suppressed and a high-temperature diffusion peak appears in the effusion spectrum. These characteristics are generally correlated to a densification of the microstructure.

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