Study of Effects of Metal Layer on Hydrogen Desorption from Hydrogenated Amorphous Silicon Using Temperature-Programmed Desorption

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1. Introduction

Hydrogenated amorphous silicon (a-Si:H) films have widely been used in solar cells and thin film transistors for liquid crystal displays. A-Si:H films are also important materials as the precursors to form polycrystalline silicon (poly-Si) films. It is well known that solid phase crystallization (SPC) is one of the useful techniques to prepare poly-Si films from a-Si:H films. Especially, metal induced crystallization (MIC) [1] and metal induced lateral crystallization (MILC) [2] have actively been investigated. These techniques have an advantageous feature, which enables to decrease the crystallization temperature by adding catalytic metals to the precursor a-Si:H films. For the preparation of a-Si:H films, low pressure chemical vapor deposition (LPCVD) [3] or e-gun evaporator [4] are usually employed. From the viewpoints of reducing the process temperature and mass production, however, it is generally understood that plasma-enhanced CVD (PECVD) is the ideal method to prepare the precursor films. The remaining problem is that the a-Si:H films by PECVD contain a large amount of hydrogen, which prevents relaxation of residual stress in the crystallization process.

It is generally known that Ni has peculiar natures to enhance decomposition of SiH_4 gas and crystallization of a-Si:H film by forming a Ni silicide, by its migration. However, there are few researches in the effects of metal layer on the desorption behavior of hydrogen from a-Si:H films. Besides, metal electrode is indispensable for the electronic devices using a-Si:H films. In this paper, we investigated the effects of various metals on hydrogen desorption from a-Si:H using temperature-programmed desorption (TPD) measurements.

2. Experiment

Si(001) wafers with 150nm-thick thermal oxides were used as substrates. A-Si:H films with thickness of 200 nm were prepared by the atmospheric pressure plasma CVD using a cylindrical rotary electrode [5]. Table I shows the deposition conditions of the a-Si:H films. To prepare the samples for TPD measurements, the substrates were cut into the size of 10 x 10 mm² after deposition of a-Si:H.

Eight kinds of metals (Al, Ni, Cu, Ge, Au, Ag, Fe, Sn) of which purities were higher than 99.99% were used in this study. These metals are usually seen as the electrode and wiring materials for the electronic devices, the catalyst for MIC/MILC, or the contaminations in a-Si:H films. The ultra thin metal layers of 5 nm thickness were coated on the

Table I	Deposition conditions of the a-Si:H films by the at-	-							
	mospheric pressure plasma CVD.								

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Carrier gas	Не
H_2 concentration (%)	9
SiH_4 concentration (%)	0.3
Process pressure (Pa)	1×10^{5}
Electrode rotation speed (rpm)	3000
Deposition gap (mm)	0.2
Input VHF power (W)	600
Substrate temperature (°C)	220
a-Si:H film thickness (nm)	200

a-Si:H films at room temperature by a vacuum evaporator. Hydrogen desorption spectra of the a-Si:H films were measured by a TPD system (ESCO: EMD-WA1000K). The base pressure of the TPD system was 1×10^{-7} Pa, and the heating rate of the samples was 30 °C/min. To exclude the influence of contamination, which might be adsorbed during the metal evaporation, a sample was loaded into the same evaporator without metal coating, and the spectrum of the sample was used for reference.

3. Results and discussion

Figure 1 shows the hydrogen desorption spectra of the sample with an Al layer (solid line) and the reference one (dotted line). In Fig. 1, the TPD spectrum of the reference sample has two principal peaks. The peak at around 350 °C is due to neighbouring Si-H bond in the a-Si:H film, while the peak at around 550 °C is attributed to isolated Si-H bond. Comparing the two spectra, it is obvious that the positions of hydrogen desorption peaks, especially the starting temperature, of the Al coated a-Si:H film drastically shift to the lower temperature side. Since the eutectic alloy formation between Al and Si occurs at a temperature as high as 577°C, the decline of the hydrogen desorption temperature is not due to the depression of melting point by eutectic reaction.

In order to evaluate the effect of Al on the hydrogen desorption quantitatively, the activation energies were estimated from Arrhenius plots for the early stage of hydrogen desorption in Fig. 1. The obtained activation energies were 0.52eV for the Al-coated sample and 1.80eV for the reference one, and the difference in the activation energies (ΔE_a) was calculated as 1.28eV. The activation energy of 0.52eV is much lower than that of hydrogen desorption from dihydride-terminated Si(001) surface (1.86 eV). It is confirmed that the Al layer have important effects on promoting hydrogen desorption from the a-Si:H film.



Fig.1 TPD spectrum of the sample with a 5nm thick Al layer together with that of the reference sample.

Table II Summary of the experimental results. (TD : Whether the temperature of hydrogen desorption decreased, ΔE_a : the difference in the activation energy for hydrogen desorption and P_R : the peeling ratio of the films after TPD measurement.)

element	Al	Ni	Cu	Ge	Au	Ag	Fe	Sn
TD	0	\bigcirc	0	×	\bigcirc	×	\bigcirc	\times
$\Delta E_{a}(eV)$	1.28	1.21	0.62	0.25	0.83	0	1.04	0.50
P (%)	0.01	0.01	0.34	5.04	0.05	9.62	0.01	0.08

After the TPD measurements, some peeling parts were seen in the reference sample, which seemed to be due to explosive outgassing of hydrogen from the film during the heating process. On the other hand, no film peeling was observed for the Al-coated sample. For other metals, the TPD measurements were carried out in the same manner. The experimental results are summarized in Table II. It is found that Al-coated sample has the largest value of ΔE_a . The peeling ratio of each sample, which is determined from the peeling area dividing by the total area of the a-Si:H film, is also shown in Table II. Figure 2 shows the relationship between the peeling ratio and ΔE_a . It is interesting to notice that the peeling ratio decreases as ΔE_a is increased.

To investigate the origin of the film peeling, the TPD measurement was performed using an a-Si:H film without metal coating formed on a bare Si(001) wafer. The result (not shown) revealed that no film peeling occurred, al-though a similar TPD spectrum to that of the reference sample was obtained. Thus, it can be said that the film peeling is independent of explosive hydrogen outgassing. Possibly, stress relaxation is induced by the metal during the hydrogen desorption process.

At the present stage, the detailed mechanism of the behavior of metals in the a-Si:H film is not clarified. However, it is believed that the metals such as Ni and Al play important roles not only in the promotion of hydrogen desorption but also in the relaxation of the residual stress by diffusing in the a-Si:H matrix. In order to better understand the detail of the metal-induced behavior of a-Si:H



Fig.2 The peeling ratios of the samples after TPD measurements as a function of ΔE_a

film, further systematic study on the relationship between the hydrogen desorption and the residual stress of the a-Si:H film is necessary.

4. Conclusions

We have investigated hydrogen desorption behaviors from a-Si:H films with various ultra thin metal layers using TPD measurements. The results were characterized by calculating the activation energy for hydrogen desorption

and by observing the peeling ratio of the film. The results showed that Al had the largest effect on decreasing the activation energy for hydrogen desorption. In addition, the peeling ratio of the film had a correlation with the difference in the activation energies (ΔE_a). These results suggested that the metals diffusing in the a-Si:H matrix enhanced not only the hydrogen desorption but also the relaxation of the residual stress.

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