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ORIGIN OF SURFACE DEFECTS IN a-Si:H FILMS

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ABSTRACT

Surface oxidation and surface defect creation processes in a-Si:H films have been studied in detail by means of electron spin resonance(ESR) and X-ray photoelectron spectroscopy(XPS). It is found that Si dangling bonds created by the surface oxidation distribute far wider than the thickness of the SiO₂ layer. These defects are also found to be removed out by annealing at around 100°C. These defects are proposed to be created by a stress in a-Si:H induced by the surface oxidation. Moreover, the presence of the surface defects unrelated to oxidation is shown for the first time by the present experiment. The origin of these defects, however, are not clear at present.

INTRODUCTION

A number of studies on the surface defects in a-Si:H films have been carried out until now. The surface defect density in a-Si:H films is known to increase when the films are exposed to air or oxygen[1-3]. The thickness of the surface defective layer was found to be of the order of 10 nm[1]. However, the details of the relation between the defect creation and the oxidation process have not been clarified.

In this paper, we study the relation between the native oxidation process and the surface defect creation in detail, so as to understand the origin of the surface defects in a-Si:H films.

EXPERIMENTAL

Measurements of the surface defects and the oxidation states were carried out by an X-band ESR and an XPS, respectively. Since the signal-to-noise ratio of the ESR signal with $g=2.0055$ which originates from Si dangling bonds is not good, the experimental error is estimated to be about 20~30%. Used X-ray source for XPS was MgK_α (1253.6eV), and the energy resolution of the electron analyzer was set between 0.8 and 1.0eV. The films with a thickness of 100nm were prepared by glow-discharge decomposition of SiH₄ on fused quartz for ESR and n⁺-type crystalline Si for XPS, using a same preparation condition as reported in ref.1. Furthermore, a film with a thickness of 2250 nm was also prepared on fused quartz substrate for photoconductivity measurement. The photoconductivity was measured with a coplanar aluminum electrode.

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RESULTS AND DISCUSSION

Figure 1 shows XPS spectra of Si 2p for various storage time when a-Si:H film is exposed to air at 20°C with 50% humidity. A peak at $\sim 99\text{eV}$ is due to a Si atom bonded to four Si atoms, and a peak at $\sim 103\text{eV}$ is due to a Si atom bonded to four O atoms (SiO_2) [4]. As seen from the figure, the intensity of the SiO_2 peak increases with increasing the storage time. However, no appreciable peaks for intermediate suboxides SiO_x [4] could be observed in the XPS spectra.

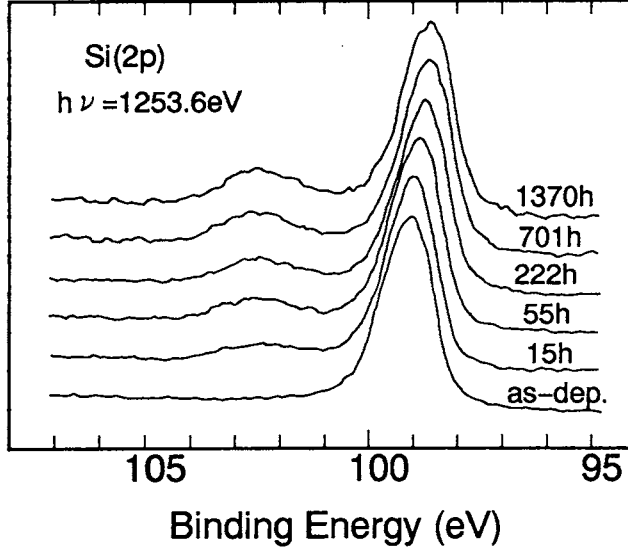


Fig.1. XPS spectra of Si 2p for a-Si:H film exposed to air at 20°C with 50% humidity for various times.

The thickness of the SiO_2 layer (D) can be estimated from the ratio of the intensity of the 103eV peak (I_{SiO_2}) to that of the 99eV peak (I_{Si}) using a following equation,

$$D = \lambda \sin \theta \ln \left[\left(\frac{n_{\text{Si}} F_{\text{Si}} I_{\text{SiO}_2}}{n_{\text{SiO}_2} F_{\text{SiO}_2} I_{\text{Si}}} \right) + 1 \right], \quad (1)$$

where λ is the mean free path of photoelectrons, θ the take-off angle of photoelectrons, n the Si atom density, F the relative response factor. Subscripts, Si and SiO_2 , denote the values corresponding to the 99eV and 103eV peaks, respectively. Values of the parameters used to estimate D are as follows; $\lambda = 2.5 \text{ nm}$ [5,6], $\theta = 90^\circ$, $n_{\text{Si}} = 5.0 \times 10^{22} \text{ cm}^{-3}$ and $n_{\text{SiO}_2} = 2.3 \times 10^{22} \text{ cm}^{-3}$ [4], and $F_{\text{Si}} = F_{\text{SiO}_2}$. Figure 2 shows the storage time dependence of D , when a-Si:H films are stored in air at two different environments, 20°C with 50% humidity and 70°C with 80% humidity. It is found that $D(70^\circ\text{C}, 80\%)$ increases faster than $D(20^\circ\text{C}, 50\%)$. For another sample exposed to air at room temperature, we found that D increases and then saturates after several thousands of hours. The saturated value of D is about 1.3 nm, which agrees well with a previously reported value of 1 nm for a-Si:H with columnar morphology [2].

Figure 3 shows the storage time dependence of the spin densities per area (N_s), when a-Si:H films are stored in the same environments as those in Fig.2. Like a behavior of the oxidation-induced change of D , $N_s(70^\circ\text{C}, 80\%)$ increases faster than $N_s(20^\circ\text{C}, 50\%)$. However, $N_s(70^\circ\text{C}, 80\%)$ starts to decrease in several ten hours and then drops to the original value within the storage time of $\sim 200\text{h}$. On the other hand, $N_s(20^\circ\text{C}, 50\%)$ continues to increase up to several hundred hours and then saturates. In case of a-Si:H films sealed in vacuum ($10^{-3} \sim 10^{-4} \text{ Pa}$), N_s

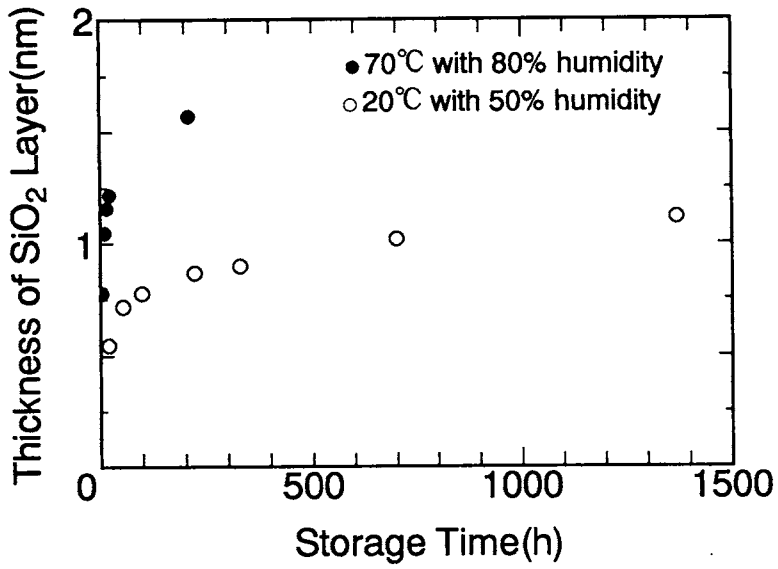


Fig.2. Storage time dependence of the thickness of the SiO₂ layer for a-Si:H films stored in air at two different environments, 20°C with 50% humidity and 70°C with 80% humidity.

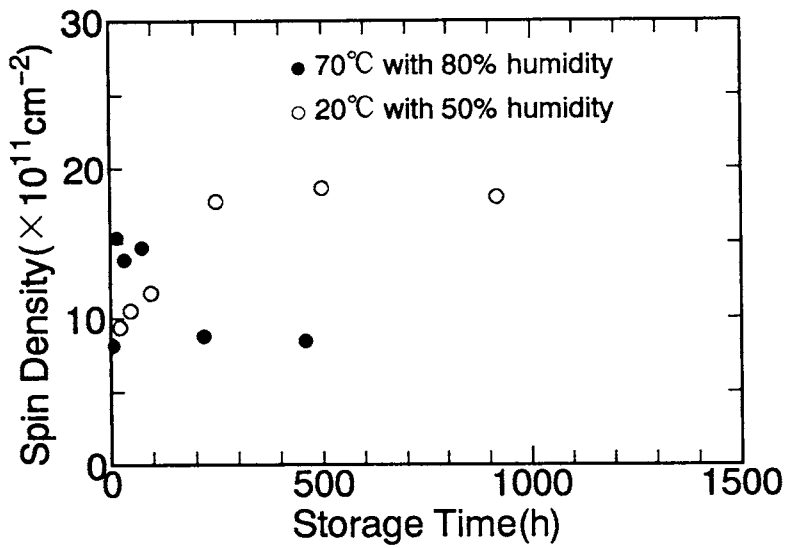


Fig.3. Storage time dependence of the spin density per area for a-Si:H films stored in the same environments as shown in Fig.2.

does not show an appreciable increase. After etching for the oxidized samples by 10% HF solution, the SiO₂ peak in XPS spectrum disappears, and the saturated N_s decreases to the value before the oxidation. From these results, the oxidation is certified as the origin of the surface defect creation[1-3]. However, for the first time, the present ESR experiment clearly shows that there exists surface defects before the surface oxidation. These defects appear to be unrelated to the oxidation.

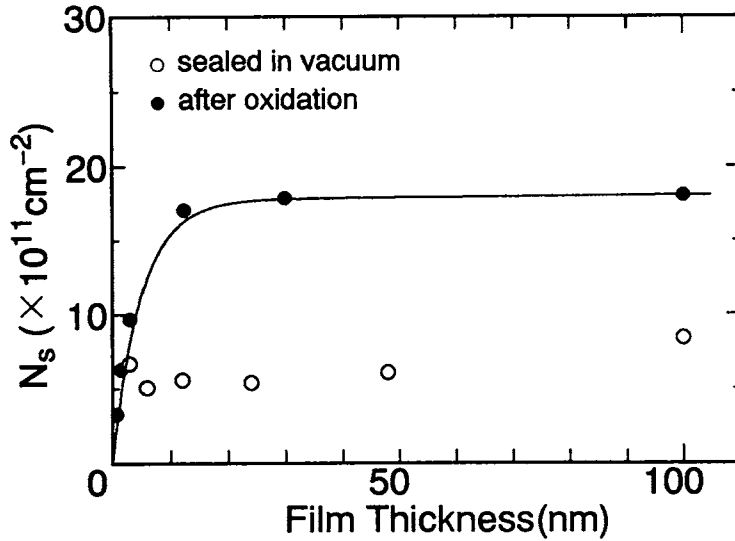


Fig.4. Film thickness dependence of the spin density per area for a-Si:H films exposed to air for more than 300 hours or stored in vacuum($10^{-3} \sim 10^{-4}$ Pa). The solid curve is drawn by eq.(2).

Figure 4 shows the film thickness dependence of N_s for the sample stored in air for more than 300h and the sample stored in vacuum. Here, the solid line is drawn by following exponential expression[1],

$$N_s = N_{sb} + N_{so} X_0 (1 - \exp(-d/X_0)) / d, \quad (2)$$

where d is the film thickness. Optimum parameters fitted to observed data are $N_{sb} = 4.31 \times 10^{15} \text{cm}^{-3}$, $N_{so} = 2.72 \times 10^{18} \text{cm}^{-3}$, and $X_0 = 5.5 \text{ nm}$. The present value of X_0 is somewhat smaller than the previous value of 12 nm[1]. However, it should be noted that the thickness of the surface defective layer X_0 is far larger than that of the SiO₂ layer D (~1 nm). The surface defect density in the samples stored in vacuum shows only a small decrease with a decrease in the film thickness until down to about 3 nm. The result means that surface defects unrelated to the oxidation distribute within 3 nm from the free surface or the interface.

It is surprising that N_s decreases after the increase in N_s for the sample stored in air (70°C, 80%) as shown in Fig.3. The reason could be attributed to an annealing effect. In order to check the possibility of annealing effect on N_s, annealing experiments are carried out for the samples

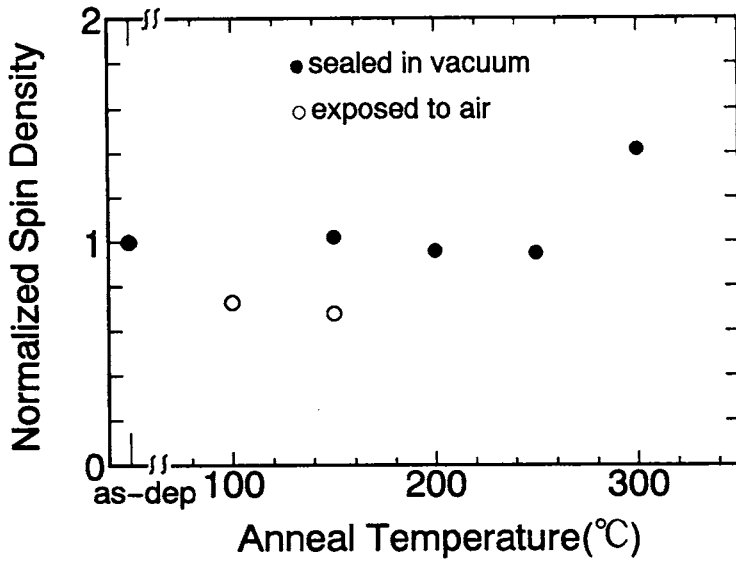


Fig.5. Annealing temperature dependence of the spin density for a-Si:H films oxidized in air or stored in vacuum.

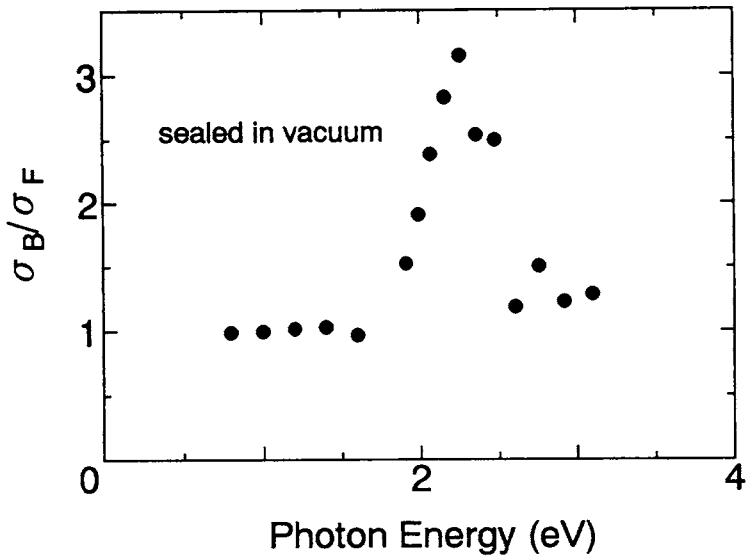


Fig.6. Ratio of σ_B to σ_F for a-Si:H stored in vacuum. Here, σ_B and σ_F are photoconductivities measured for the sample illuminated from the fused quartz side and the film side, respectively.

with the saturated value of N_s . Figure 5 shows the annealing temperature dependence of N_s . The results for the samples stored in vacuum are also shown for comparison. Here the annealing time is 30min for each point. For the samples stored in air, N_s decreases largely with annealing. On the contrary, N_s for the samples stored in vacuum remains unchanged up to 250°C and then increases at 300°C.

We try to propose a possible model for the surface defect creation by the oxidation agreeing with the experimental results mentioned above. Since the Si atom density in the SiO_2 layer is smaller than that in a-Si:H films, the conversion of Si to SiO_2 will cause a volume expansion due to surface Si-O-Si bridgebonds formation. So, it is possible that a tensile stress, near the interface between the SiO_2 layer and a-Si:H film, could be brought about close to a-Si:H film side during the oxidation, creating Si dangling bonds in a-Si:H films close to the SiO_2 layer. Then it is reasonable that the thickness of the surface defective layer is far larger than that of the SiO_2 layer. The fact that the g-value of the defects is the same as that of Si dangling bonds in a-Si:H is consistent with the present model, because the defects do not exist in oxidized layer but in a-Si:H films. The decrease in N_s by annealing can be explained by considering that the stress induced by the SiO_2 formation is relaxed by annealing, causing a decrease in N_s . In the same context, the change in N_s for 70°C-processed film shown in Fig.3, is brought by the competition between the increase in stress at the interface by the oxidation and the release of the stress by annealing.

In order to see whether the defects unrelated to oxidation locate near the free surface or near the interface between a-Si:H and the fused quartz substrate, we measured the photon energy ($0.6\text{eV} \leq h\nu \leq 3.1\text{eV}$) dependence of the photoconductivity, with the samples illuminated from the fused quartz side (σ_B) or from a-Si:H film side (σ_F). The result is shown in Fig.6. Since the light penetrates almost homogeneously into the films in a lower photon energy ($h\nu \leq 1.6\text{eV}$) region, $\sigma_B/\sigma_F = 1$. However, the σ_B/σ_F is found to be larger than 1 in the region of $h\nu > 1.8\text{eV}$ where the light can only penetrates shallower than the film thickness. $\sigma_B/\sigma_F > 1$ suggests that the free surface layer has a larger density of defects than the interface layer. It might be possible that these defects are related with hydrogen-rich layer at the growing surface as suggested by Jin and Ley[7]. However, the possibility appears to be unlikely because these defects after the oxidation in the environment (70°C, 80%) for more than 200h remain the same density as shown in Fig.3. Therefore, the origin of these defects is not clear at present.

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