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In-situ XPS Characterization of Amorphous Semiconductor Hetero-junction Prepared by Photo and Plasma CVD Method

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The heterojunction interface of an amorphous semiconductor bilayer (c-Si/a-SiC:H:F/a-Si) has been analyzed with an atomic scale resolution by using insitu XPS. The intensity of photoelectrons originating from C and F in the a-SiC:H:F and transmitting an a-Si:H deposited on the a-SiC:H:F was measured as a function of the a-Si:H layer thickness. For two types of bilayers fabricated by such two different methods as the batch method and the continuous method, the XPS analysis indicates that the interface fabricated by the batch process is ideally sharp and that by the continuous method has compositional transition region of about 5A thick.

1. INTRODUCTION

Amorphous semiconductor multilayer films with hydrogenated amorphous silicon as one of the components are of current interest because not only of their possibility for the practical devices, but also of their usefulness for studying the interfaces between the layers. Especially, the interface flactuations such as the sharpness of compositional alternation and the flatness of the interface have been attracted much interest and studied in detail by using TEM¹⁾, IR absorption²⁾, Raman spectra³⁾, optical absorption⁴⁾, ellipsometry⁵⁾ and so on, because the interface give decisive effects on the properties of the films as the component layers thicknesses decrease. In this study, amorphous semiconductor heterojunction interface was analyzed with an atomic scale resolution by a novel method using in-situ XPS. One of the two types of hetero-bilayers was fabricated by the conventional batch method including the evacuation of the reactor before the second layer deposition. The other was fabricated by the continuous method in which our novel concept for continuous multilayer deposition named Pulsed Plasma and Photo (PP&P) CVD was used^{6,7)}. The interface structure was characterized by analyzing the intensity dependence of photoelectrons originating from the bottom layer and escaping an inelastic collision in the upper layer.

2. EXPERIMENTAL

To obtain the in-situ data, a PP&P CVD apparatus which enabled double excitations both by the UV-light irradiation from a low pressure mercury lump (185, 254nm) and by the inductivly coupled plasma (13.56MHz) was directly connected to an XPS analyzer (JEOL JPS-80) through a gate valve and specimen transfer system, as shown in Fig.1. At first, a-SiC:H:F (200A) was deposited on single crystal Si by plasma and photo hybrid CVD using a mixture of $Si_2H_6(3 \text{ sccm})$ and $CF_{\Delta}(60 \text{ sccm})$ at a deposition rate of 0.18A/s. Then, a-Si:H (5-50A) was accumulated on it by the mercury sensitized photo CVD using the same gas mixture at a deposition rate of 0.12A/s. The substrate temperature

and the reaction pressure were 300°C and 700 mTorr, respectively. Figure 2 shows the time chart of excitation process employed to deposit these bilayer films. In the batch process, the film deposition was stopped and the source gas mixture was evacuated between the depositions of a-SiC:H:F and a-Si:H layers. The other is the continuous process in which only rf power was turned off when the a-SiC:H:F bottom layer of 200A had been deposited to form the a-Si:H top layer continuously by the sustained photo excitation. The deposited specimen was brought to the analysis chamber $(2x10^{-7}Pa)$ by the transfer system without being exposed to air. The X-ray of Mg Ka (1254eV) was irradiated to the specimen and the generated photoelectrons were detected in the direction normal to the specimen surface. The photoelectron intensities were evaluated by the integrated area of the XPS peaks of C 1s and F 1s core levels.

3. RESULTS

The logarithm of the photoelectron intensities for C ls and F ls was plotted against the a-Si:H top layer thickness d for the specimen prepared by the batch method is shown in Fig.3(a). The plot for the specimen prepared by the continuous method is depicted in Fig.3(b). Plots for the batch method gave straight lines, whereas Fig.3(b) shows an apparent deviation of the plots from the straight lines in the small d region.

4. DISCUSSION

Under the conditions of present XPS measurement, the X-ray penetration depth is considered to be much longer than the film thickness. Assuming that the inelastic collision probability of the photoelectron is constant, ideal interface without any fractuation shoud give the relationship :

 $I(d) = I(0) \exp(-d/\lambda)$ ---- (1)

where I(d) is the intensity of photoelectrons originating from the core level of carbon or fluorine in the bottom layer and escaping through the top layer (thickness of d) and λ is the mean free path of photoelectrons in the top a-Si:H layer.

Figure 3(a) shows the plot for the interface prepared by the batch method. The linear relationship clearly indicates that the interface fabricated by batch process is ideally sharp. The slopes of the plots of Fig.3(a) give the mean free paths of 12.6A and 8.8A for the photoelectrons of C 1s and F 1s, respectively. Fig.3(b) shows the plots for the interface fabricated by the continuous method. The observed nonlinear relationship suggests the existence of the interface fluctuation.

As the origin of interface fluctuation of the bilayer made by the continuous method, the following three possibilities shoud be taken into account.

[1] Perturbation of the interface plane flatness. This phenomenon has been often shown in cross sectional TEM photograph of amorphous semiconductor superlattices.¹⁾ See Fig.4(b).

[2] The presence of interface region with gradient compositions made by the interdiffusion or cross contamination. See Fig.4(c).

[3] Non-uniformity of the top layer thickness. See Fig.4(e)

Combination of these three factors (expressed "yes" or "no" in Fig.4 depending on the presence or absence of each fluctuation factor) can give eight types of bilayer structures listed in Fig.4

The relation between the photoelectron intensity and the top layer thickness should reflect the depth profile of the probe elements (C or F) from the edge of the bottom layer into the top layer in the direction normal to the substrate surface. Hence, the influence of the factor [1] does not make a difference in the above rerationship. The structures shown in Fig.4 (a) and (b) give the same log(I(d)) vs d relationship as is shown in Fig.3(a). The bilayer structure depicted in Fig.4 (c) and (d) will shift the linear part of log(I(d)) vs d relationship rightward as much as the effective interface plane is floated into the top layer by the contamination. Such relationship as solid lines in Fig.5(a) will be obtained parallel to the dotted line which correspond to the ideal interface. The island like nucleation with the covering fraction of r and the island height of d/r gives the relationship of broken line in Fig.5(b). Since r could increase and the uniformity of top layer thickness might be improved with the increase of d, the observed data should deviate from the dotted ideal line relatively large in the small d region and approach to the ideal line with the increase of d as is indicated by the solid line shown in Fig.5(b).

Judgeing from the linear log(I(d)) vs d plots derived from the batch method bilayer (Fig.5(b)), it is concluded that the interface is very sharp in compositional change and the island like nucleation growth is not probable. The data in Fig.5(a) obtained from the continuous method bilayer show a straight line parallel to the ideal line. Thus the cross contamination region should exist at the interface. The concentrations of C and F were assumed to decrease exponentially with the specific length of ℓ , which is defined as $I(d+\ell)/I(d) = 1/e$. Then the photoelectron intensities should be represented as:

$$I(d) = I(0) \left(\frac{\lambda}{\lambda - \ell} \exp(-\frac{d}{\lambda}) - \frac{\ell}{\lambda - \ell} \exp(-\frac{d}{\ell})\right)$$

The least square fitting of this equation to the observed plots gave $\ell = 4.7A$. This length corresponds to two or three atomic layers of silicon and may represent the thickness of boundary layer where the growing surface is reluxed and stabilized into amorphous film. Thus, in-situ XPS has been verified to provide useful information on the interface fluctuation with atomic scale resolution.

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Fig.1 Schematic representation of sample preparation chamber and XPS analysis system.



Fig.2 Time chart for deposition and analysis of c-Si/a-SiC:H:F/a-Si:H layered films. (a) batch method (b)continuous method.



Fig.3 Photoelectron intensities generating from C ls and F ls core levels in the bottom layer for various top layer thicknesses. (a) For the bilayers prepared by batch method. (b) For continuous method bilayer.



Fig.4 Schematic representation of eight types of interface structures classified by three interface fluctuation factors, [1] perturbation of interface flatness, [2] gradient composition change, and [3] Nonuniformity of top layer thickness.



Fig. 5 The log(I(d)) vs d relationships for the structures depicted in Fig.5. (a): for Fig.5 (c) and (d), & is effective thickness of interface region; (b): for Fig.5 (e) and (f), r is covering fraction. The data for F showed in Fig.4 are replotted.