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Spectroscopic Ellipsometry for the Identification of Paracrystallites in the Ultra-Thin Thermal CVD Hydrogenated Amorphous Silicon Films

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1. Introduction

Recently, the enlightenment of higher order atomic correlation functions has insight into the medium range order (MRO) of disordered materials [1]. In this regard, image statistics in the high resolution transmission electron microscopy and accurate pseudo-potential calculation of atomic bonds at the interfaces of amorphous films are needed [2]. This is a form of mesoscopic averaging through a volume characterized laterally by the microscope resolution and vertically by the specimen thickness containing 1000 atoms. So far, spectroscopic methods, which average out the macroscopic phenomenon, cannot identify MRO in the amorphous network unambiguously. In this report, we will show for the first time that ellipsometric spectra of ultra-thin thermal CVD hydrogenated amorphous silicon (a-Si:H) films, deposited on c-Si/SiO_2 substrate, is indicating the presence of MRO.

2. Experimental

The ultra-thin a-Si:H films were deposited by the thermal chemical vapor deposition at 459 °C onto the HF treated SiO_2/c-Si substrates. Disilane (Si_2H_6; 2cc/min) and hydrogen (H_2; 100cc/min) were the process gases for deposition. Here hydrogen was mainly used just as a diluent for the precise control of low deposition rate, typically 8.8 Å/min, since the dissociation energy of H_2 molcule is rather high compared to the substrate temperature. Chamber pressure was fixed at 18 Torr. Bonded hydrogen content of such films were less than 3 at%.

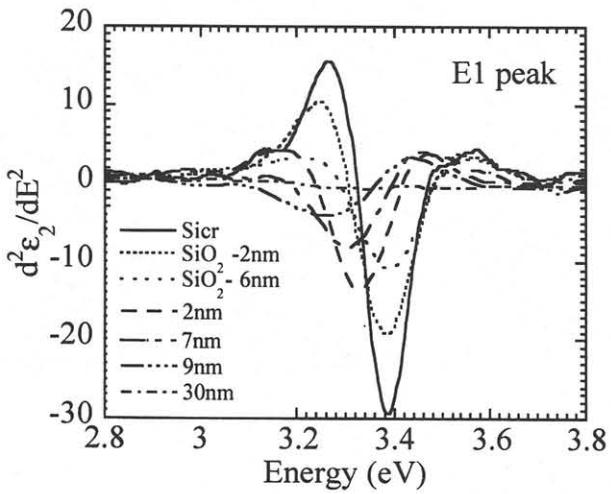

Figure:1 $d^2\varepsilon_2/dE^2$ spectra for the ultra-thin a-Si:H films

The spectroscopic ellipsometry (SE) measurements were carried out over the spectral range of 0.24 – 0.84 μm using a spectroscopic ellipsometer (SOPRA Co.) at an angle of incidence of 75°. The optical train contained a Xe lamp (75 W), an optical bench, a rotating polarizer, a sample table, a fixed analyzer, a fiber optic cable and a photo multiplier tube. GESP5® (version 6.0) software was used for the data acquisition and the data analysis was done by using Winelli software® (version 4.04). Optical properties, viz., dielectric constants (real part; ε_1 and imaginary part; ε_2) of ultra-thin films were obtained from the bulk calculation of ellipsometric parameters (Ψ and Δ). To find out the critical transitions (E1 and E2) of c-Si substrate as well as ultra-thin films, second-order derivation and successive smoothing of ε_1 and ε_2 spectra were done using Savistzky Golay Algorithm (3 × 8).

3. Results and discussions

Most commonly, E1 and E2 transition peaks for c-Si are designated from $d^2\varepsilon_2/dE^2$ and $d^2\varepsilon_1/dE^2$ respectively [3]. In the polycrystalline silicon films, surrounding environment (void, amorphous part) can affect more severely E2 peak than E1 peak of c-Si. So here we have only concentrated on E1 peak of ultra-thin films. Figure 1 shows $d^2\varepsilon_2/dE^2$ spectra in the energy range 2.8 to 3.8 eV to identify the E1 peak for the ultra-thin a-Si:H films. The central position of E1 transition for the ultra-thin film with thickness of 9nm is 3.259 eV whereas that for c-Si is 3.380 eV. Decreasing thickness of a-Si:H films E1 peak shifts to the higher energy side of $d^2\varepsilon_2/dE^2$ spectra. For the film thickness of 2 nm E1 transition center is 3.326 eV, close to the E1 peak center of c-Si. However, this peak disappears for the film with thickness of 30nm.

Either (i) interface stress between c-Si and amorphous matrix [4] or (ii) the presence of paracrystallites [5] (MRO) in the ultra-thin a-Si:H films may result in this peak, different from the usual E1 peak for c-Si. No significant peak shift is observed with the increase of thickness of thermal SiO_2 on c-Si substrate [Figure 1]. So reason (i) might be eliminated. Reason (ii) is more feasible. Nakagawa et. al. [6] fabricated crystalline silicon dots on the HF treated c-Si/SiO_2substrate at temperature above 500 °C. In our work, substrate temperature is 460 °C and our speculation is that HF treated SiO_2 substrate can initiate the formation of deformed crystalline network at this temperature. Due to the random distribution of the MRO in the ultra-thin films SE can identify the corresponding E1 transitions. It has been

reported that the formation of paracrystallites at the interface of the substrates and a-Si:H films is possible through the chemical etching by hydrogen atoms [7]. With the increase of the thickness of ultra-thin a-Si:H films, the size of the paracrystallites increases and E1 peak shifts to the lower wavelength side. Typical size of the paracrystallites is in the range of 5 to 20 Å [2]. The disappearance of E1 peak above the thickness 30 nm can be explained as follows: with the increase of the film thickness, amorphous matrix dominates over the deformed crystallites and macroscopic averaging ellipsometric spectra cannot reveal the presence of paracrystallites.

Moreover, after annealing of any a-Si:H film, new peak shifts to the higher energy side irrespective of the film thickness due to the reduction of the degree of MRO. In Figure 2, such shift of E1 peak for a-Si:H film of 9nm in thickness after rapid thermal oxidation (RTO) or rapid thermal annealing (RTA) is displayed. It is reasonable because short range order occurs at the expense of MRO by the thermal annealing [2]. Not only the peak shift, but also two new peaks appear that are marked by the arrows. Peak position of such peaks is higher than that of E1 transition of c-Si (3.380 eV). After RTO/RTA, ultra-thin films contains a distribution of nanocrystalline dots and these marked peaks can be the result of quantum size effect in the nanocrystalline dots of the ultra-thin films [8].

4. Conclusions

Morphology of ultra-thin (2-30nm) a-Si:H films have been studied by the spectroscopic ellipsometry. Indication of E1 transitions in the $d^2\varepsilon_2/dE^2$ spectra intimates the presence of paracrystallites in the ultra-thin films, which cannot be revealed by ordinary transmission electron microscopy. HF treated SiO_2/c-Si substrates may help to form randomly distributed deformed crystallites in the ultra-thin a-Si:H films. Spectroscopic ellipsometry can identify the E1 transitions from deformed crystallites, although it is a method of macroscopic averaging. Thermal annealing reduces this medium range order in the ultra-thin films.

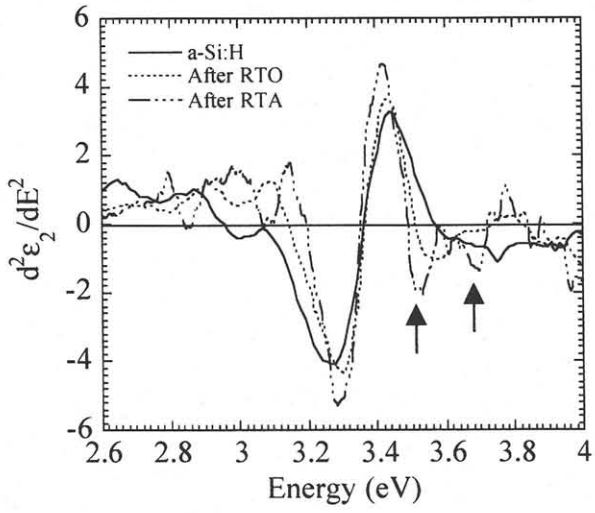

Figure: 2 $d^2\varepsilon_2/dE^2$ spectra for the ultra-thin films with the thickness of 9 nm. The arrows represent the peaks coming from nanocrystalline Si.

Acknowledgments

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