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THE NATURE OF INTERMEDIATE RANGE ORDER IN Si:F:H:(P) ALLOY SYSTEMS

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Abstract.- Our investigation of intrinsic-Si:F:H alloys have shown them to be totally amorphous with no detectable intermediate range order or microcrystalline phase using TEM, and Raman techniques. We report our investigation of highly P-doped Si:F:H alloys having an intermediate range order. The characteristic length of this order is 20 to 60Å. Transmission electron microscopy is used to corroborate the particle size, and the volume fraction of crystallinity in a two-phase system, determined by Raman scattering. Transmission electron diffraction indicates that the structure is similar to micro-crystals. Unlike conductivity, electroreflectance response does not depend on the critical volume fraction of crystallinity in a percolation process. The high conductivity and low optical absorption for these P-doped Si:F:H alloys are ideal properties for contact layers in an a-Si:F:H solar cell.

Introduction.- Previously, we have reported, in heavily As- or P-doped Si:F:H alloy systems, the appearance of a Raman peak lying intermediate between 522 cm⁻¹ for c-Si, and 480 cm⁻¹ for amorphous-Si(1), (2). Whenever such Raman peak is observed, electrolyte-electroreflectance (EER) peaks appear around 2 eV, together with those associated with c-Si at 3.4 eV and 4.5 eV. We have explained these observations in terms of an intermediate range order or a "microcrystalline phase". Nowe we have found similar observations in moderately P-doped samples. On glass substrates EER may be observed when the volume fraction of crystallinity has passed 0.16, the critical density, ρ_cr, in percolation processes (3), (4). However, on stainless steel substrates, EER has been observed for ρ_cr < 0.16, indicating that unlike conductivity, EER requires only the existence of relatively sharp electronic density of states. Extensive structural studies indicate that this intermediate order is distinct from amorphous state and is similar to the microcrystalline state discussed by Moss and Graczyk (5). Transmission electron diffraction shows that the first, second and third rings coincide with those of (111), (220) and (311) of crystalline silicon. The average particle size determined from Raman peak position gives 20 to 60Å. Particle sizes in this range or even smaller have been reported by Goodman (7), however, substantial amounts of oxygen were introduced in silicon. Therefore, our samples offer a unique opportunity for the investigation of small particle and grain boundary effects.

Subsequent to our report on the As-doped Si:F:H alloy system (8), Tanaka et al. (9) reported the observation of a crystalline phase in highly P-doped Si:F:H. Applying higher RF-power, Hamasaki et al. (10) has produced crystallization in P-doped a-Si:H. It is important for us to point out that the occurrence of crystallinity in fairly heavily n-doped region is actually desirable for solar cell purposes because of higher electrical conductivity and lower optical absorption. The latter property allows maximum light transmission through the contact to the intrinsic Si:F:H which is without trace of crystallinity.
Results and Discussions. - Our Si:F:H(P) samples are prepared by a glow discharge decomposition of SiF$_4$ and H$_2$. Phosphorus doping is introduced by mixing PH$_3$ with the gas mixture having the ratio of PH$_3$ to SiF$_4$ between 20 to 500 ppm. Composition is determined by Auger, SIMS and resonant nuclear reaction (11). Typically, our films contain 1-4% of F, 4-6% of H, and 1-10% of P. Fig. 1 shows the measured Raman linewidth $\Delta \omega$ versus the Raman frequency. Note that the crystalline Raman peak at 522 cm$^{-1}$ for Si is shifted down to peak position as low as 508 cm$^{-1}$ due to small particle size effects or possibly also by strain. On the other hand, the amorphous peak, marked a, has a linewidth of $\approx 80$ cm$^{-1}$ centered at 480 cm$^{-1}$. The sputtered a-Si has noticeably broader linewidth and lower Raman frequency. Also plotted in Fig. 1 is the particle size $\lambda$ versus frequency, obtained from $\lambda \sim 2\pi/k$ using the phonon dispersion curve from neutron scattering (12). Thus, we found that the particle size of our microcrystalline is in the range of 20 Å to 60 Å. It is significant that no Raman peak has been found between 483 cm$^{-1}$ and 508 cm$^{-1}$, indicating the absence of a continuous transition.

Figure 2 shows a typical TED, (a); and TEM, (b). Note that the second amorphous ring lies between the (220) and (311) of c-Si. The diffraction pattern is a superposition of c-Si and a-Si. In the bright field TEM micrograph (b), there appear clusters of few hundred anstroms. However within each cluster, there are fine structures of the order of 50 Å. Therefore, the particle size in Fig. 1 corresponds to the fine structures in TEM.
The Raman spectrum of a typical SiFxH(P~1%) sample, shown in Fig. 3, may be resolved into an amorphous component, marked a, and a crystalline component having a peak at 519.5 cm\(^{-1}\). The plasma line of the Ar-laser at 19750 cm\(^{-1}\) is left in during the measurements as an accurate calibration for the Raman frequency. The volume fraction of crystallinity for this sample is found to be, \(\rho_v \approx 0.25\). Since the critical density in percolation processes for these samples was determined to be 0.16 (3), this sample is highly conductive having \(\sigma \approx 4\) (ohm cm\(^{-1}\)), and shows EER response in spite of the use of a glass substrate. Note that this two-phase behavior was not seen on the samples reported in Ref (1) and Ref (2), because in our previous investigations, we dealt with essentially single-phase "microcrystals", having \(\rho_v\) much higher. From the preparation point of view, in addition to lower phosphorus contents, these two-phase samples are generally thinner, having thicknesses \(\approx 600\) Å.

Part of our present success in identifying the nature of these films is due to the extreme sensitivity of Raman scattering. We are able to produce a good Raman spectrum of a film no thicker than 200Å. These thinner films also yield better transmission electron micrographs and diffraction rings.

Fig. 4 shows the EER response of two groups of samples, one on glass substrates, and the other on stainless steel substrates. For the former, EER is strong for \(\rho_v = 0.24\) taken at 3 s time constant; and weak for \(\rho_v = 0.2\) which required a 30 s time constant to show up the usual 3.4 eV structure. For \(\rho_v = 0.08\), which is below the percolation limit, no EER response was observed. On the other hand, for the latter samples, EER response is strong for both samples, \(\rho_v = 0.17\) and 0.08, above and below the critical density for a percolation process. Note that the usual structure near 2 eV, 3.4 eV and 4.5 eV are essentially similar to those reported by us previously. The difference between the two groups can be understood. In order to apply a high electric field for these samples on glass substrates, one of the two electrodes was on the film itself therefore requiring conductivity; whereas, on stainless steel, the metal serves as one of the two electrodes which does away the need for higher conductivity. Therefore our results indicate that EER response, unlike conductivity, does not depend on percolation processes. In fact, as long as there exists a sufficient amount of microcrystals, EER response should appear whenever a high electric field can be applied.

Conclusions.- To summarize, we have now specified in detail the nature of the intermediate range order in our SiFxH(P) samples. The range is approximately 20 to 60Å, having TED similar to microcrystals. The combination of Raman scattering and EER provides us means to make detailed studies. The minimum detectability of
trace crystallinity appears to be about 2% crystallinity. On the other hand, EER may ultimately be a very sensitive tool to detect trace crystallinity. Unlike Raman measurements, at present EER does not give a quantitative determination of crystallinity. However, the possibility of using EER to study the electronic structure of these extremely small particles should be very valuable.

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Fig. 4 EER spectra of two types of samples: Top, on glass; and bottom, on stainless steel substrates. The electrolyte was 0.001 N solution of KCl. Modulating frequency is between 17 to 36 Hz. The time-constant used was 3 s, however, 30 s was used for weak and noisy responses.

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