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PHOTOEMISSION STUDIES OF THE TRANSITION FROM AMORPHOUS TO MICROCRYSTALLINE SILICON

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Abstract. - We have studied a series of samples spanning the range from purely amorphous to microcrystalline silicon prepared by chemical transport in a hydrogen plasma or by sputtering in a H₂/Ar mixture. The first order Raman spectra show a superposition of amorphous and crystalline contribution, showing some features of wurtzite-silicon. The electronic density of states, as deduced from X-ray photoelectron-spectroscopy, shows a gradual change from microcrystalline structure for samples prepared by chemical transport to the amorphous DOS for samples sputtered in pure argon.

Introduction. - Thin film microcrystalline silicon (μc-Si) is in some respects an intermediate phase between monocrystalline silicon (c-Si) and amorphous silicon (a-Si). There have been a number of attempts to explain physical properties of a-Si by means of microcrystal models. It has been established that the dilution of SiH₄ species with hydrogen in the plasma favours the formation of microcrystals even at temperatures below 300°C.¹,²

We present here a new approach to the preparation of μc-Si based on the sputtering process. By varying the H₂-concentration in a H₂/Ar sputter gas, we obtain Si-films at 250°C that range from a-Si to μc-Si, as shown by their Raman spectra. This continuous transition offers the unique possibility to study the changes in electronic structure of these specimens through photoelectron spectroscopy.

Preparation. - For the preparation of the μc-Si sample, we used the following two methods:

1. Chemical transport in hydrogen plasma onto substrates held at 300°C, as described in¹,³
2. reactive DC-sputtering of a silicon-single-crystal target (n-type, 8.10¹³ cm⁻³) in a mixture of H₂ and Ar, total pressure 0.1-0.2 mbar. The substrates were held at 250°C; the target diameter was 30 mm at a distance of about 25 mm from the substrate; the discharge current was kept at 2mA and the voltage between 1 and 2 kV.

In the same reactor we produced a-Si by either sputtering in pure Ar or decomposing SiH₄ in a DC-plasma onto substrates kept at room temperature. All the samples were deposited on stainless steel and on silicon-single crystal substrates. They were transferred under vacuum into a HP 5950 A XPS-spectrometer within a few minutes. No contamination of oxygen, carbon or other elements were detected in any sample referred to here.

First-Order Raman Spectra. - The first order Raman spectrum provides a convenient method for determining whether a silicon film is crystalline or amorphous: a-Si yields a broad hump at 480 cm⁻¹, while c-Si yields a single sharp line at 522 cm⁻¹. In μc-Si (5 to 20 nm linear dimension of the crystallites) prepared by chemical transport⁴,⁵,⁶ or by laser annealing of a-Si⁷, the 522 cm⁻¹ line is broadened up to a factor of 2 and shifted to lower energies by up to 7 cm⁻¹ with decreasing crystallite size.
These effects have been explained by a thin slab model or by a \( q \)-vector relaxation model and will not be discussed further here. In Fig. 1 the Raman spectra for some of the films are plotted. All spectra were taken under the same conditions: 0.2 W laser power, 5145 Å wavelength, cylindrical optics was used to avoid heating by the incident laser light, spectrometer resolution 4 cm\(^{-1}\) (2 cm\(^{-1}\) for samples a, b).

**Fig. 1:**
First-Order-Raman-Spectra of diverse silicon sample.
The letters refer to Fig. 2. For clearness all the spectra (except g) have been aligned at the maximum. The energy scale therefore refers only to the c-Si sample.
In e' and f' the amorphous-contribution has been subtracted. The arrow marks the hump at 495 cm\(^{-1}\) characteristic for wurtzite Si.

For convenience the peaks (except for a-Si) are aligned at 522 cm\(^{-1}\). In spectra c, e, f two major features can be distinguished: a relatively sharp line centered at about 520 cm\(^{-1}\) and a long intense tail stretching to 400 cm\(^{-1}\). The sharp line is attributed to the scattering from the microcrystallite, while the other part is due to amorphous-like material between the crystallites.

From a comparison of the intensities of the crystalline and amorphous signal, taking the Raman cross sections into account, we estimate that the amorphous phase amounts to \( \%20\% \) in sample c and \( \%40\% \) in sample d, e and f.

We find a third component with a hump at 495 cm\(^{-1}\) in curve f. This structure is enhanced in curve f', which is the difference between f and g after g was scaled to be the same as f at 400 cm\(^{-1}\). This peak is characteristic of wurtzite microcrystals. This is evidence for wurtzite-like structures in sample f and probably to a lesser extent in the other specimens.

**XPS-Valence Band-Spectra and Electronic Density of States.** - The XPS-valence band (VB) spectra (excited with \( h\nu = 1486 \) eV) reflects the electronic density of states (DOS) of the VB, aside from photoelectronic cross section variations. By folding the calculated DOS with the spectrometer resolution function, the spectra show a very good agreement between theory and experiment especially for Si and Ge.

An advantage of using XPS in the present context is that the cross section of hydrogen induced states is negligible compared to that of the Si-states. Therefore the Si partial density is measured.

In Fig. 2 the XPS-VB-spectra for several Si samples are shown, ranging from single crystal at the top to a-Si and a-Si:H at the bottom. The spectra are aligned at the top of the VB.

Spectra a(c-Si) and b(\( \mu \)-c-Si, chemical transport) exhibit the three peak structure that is characteristic for the DOS of c-Si. This means that within our resolution (0.6 eV) there is no difference between the DOS of single crystal Si and of \( \mu \)-c-Si prepared by chemical transport.
Fig. 2:
XPS-Valence band-Spectra of diverse Silicon-samples
a: c-Si filed in UHV
b: µc-Si prepared by chemical transport
c-g: Si prepared by sputtering in H₂/Ar-atmosphere
  H₂-concentration 50%, 10%, 5%, 2.5%, 0%
h: a-Si:H prepared by DC-glow-discharge in SiH₄ at room-temperature
  for details of preparation see text.
All the spectra have been smoothed by using the same Fourier-filter procedure. There is no correction for inelastic electron background.

Spectrum g (a-Si) and h(a-Si:H) are virtually identical. They are characteristic for the DOS of a-Si in which peaks II + III have merged to form a single broad hump. The incorporation of hydrogen along apparently does not lead to a sufficient relaxation of the amorphous network to alter the DOS significantly. Revesz deduced from X-ray scattering data that a-Si should undergo a transition from a diamond-like structure to a BC-8-like structure when about 10% hydrogen is incorporated. This change in structure, if it occurs, does not affect the VB-spectrum. It remains in doubt, however, whether the DOS of the two structures (diamond and BC-8) are sufficiently different to be observable with the resolution of 0.6 eV achieved here.

Curves f to c show the VB-Spectra of sputtered Si-films with increasing H-concentrations in the sputter gas. Increasing H-concentration leads to a continuous transition towards the spectrum of c-Si. These changes reflect modifications in the Si partial density of states since the H Is states have negligible photoelectric cross sections, as mentioned above. Starting with spectrum c, peak II decreases in intensity until in the a-Si sample, it has nearly disappeared. Simultaneously the minimum between III and II is filled in. Peak I varies only a little; the VB-edge steepens from c-Si to a-Si. The gradual disappearance of II and the steepening of I cannot be explained by a superposition of the crystalline and the amorphous spectra alone. In samples d to f the amount of amorphous material is about the same, as judged from Raman spectra, while the VB-spectra change considerably.

Peak II is caused by a very sharp maximum in the DOS of c-Si due to flat bands near L and X in the Brillouin zone. A loss in long range order broadens and diminishes the sharp maximum in the DOS. In this sense, the gradual loss of peak II reflects a decrease in the size of the crystallites.

Changes in the short or intermediate range order have been considered by Johannopoulos et al. using crystalline polymorphs of Si as models for a-Si. They argued that the presence of 5 and 7-fold rings in a-Si is the main cause of the merging of peak II and III.

While this might be the case in a-Si, we would like to suggest that the increased density of wurtzite like structure elements seen in the Raman spectra of the sputtered films contributes to a reduction in peak II. Fig. 3 compares the broadened DOS of the diamond and wurtzite structures of Si. In the wurtzite structure, peak II is smaller relative to peak I and the valley between II and III is also reduced.

Fig. 3: 
Comparison of the broadened DOS of the diamond and wurtzite structures of Si. In the wurtzite structure, peak II is smaller relative to peak I and the valley between II and III is also reduced.
Fig. 3: Calculated DOS for diamond-like-Si (1) and wurtzite-like-Si (2) taken from\textsuperscript{1}\textsuperscript{1} folded with a Gaussian-distribution of 1.6 eV FWHM.

Conclusion. - We have shown that Si-films with properties intermediate between those of μc-Si and a-Si can be made by varying the H\textsubscript{2}/Ar ratio in a sputter atmosphere. The Raman-spectra are explained by a superposition of amorphous and crystalline parts. The latter show some of the characteristics of the wurtzite-structure. The VB DOS progresses from the 3-peak structure of c-Si to the 2 peak-structures of a-Si as preparation conditions are altered. This change can be explained by increasing portions of a-Si in the material as well as increasing wurtzite-like regions.

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Literature.