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HAL Id: jpa-00220912

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Submitted on 1 Jan 1981

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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, 8.10¹⁹ 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 2 mA 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 transport⁴⁵ 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 crystal-lite size.
These effects have been explained by a thin slab model\textsuperscript{8} or by a $q$-vector relaxation model\textsuperscript{6} 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 clear-ness 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.\textsuperscript{6}

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 $\approx$20\% in sample c and $\approx$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.\textsuperscript{10}

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.\textsuperscript{11} 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(µc-Si, chemical transport) exhibit the three peak structure that is characteristic for the DOS of c-Si.\textsuperscript{14} This means that within our resolution (0.6 eV) there is no difference between the DOS of single crystal Si and of µc-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 H$_2$/Ar-atmosphere
   - H$_2$-concentration 50%, 10%, 5%, 2.5%, 0%
h: a-Si:H prepared by DC-glow-discharge in SiH$_4$ 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 back-ground.

Spectrum g (a-Si) and h(a-Si:H) are virtually identical. They are characteristic for the DOS of a-Si in which peaks I$_1$ + I$_{III}$ 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 charges 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 Johnopoulos 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:
Calculated DOS for diamond-like-Si (1) and wurtzite-like-Si (2) taken from 
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 H₂/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.

Acknowledgements. - We thank Z.P. Wang for help with the Raman-measurements, and W. 
Neu for his technical assistance during the film preparation.

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