GROWTH OF PLASMA-TRANSPORT MICROCRYSTALLINE SILICON AS STUDIED BY IN-SITU RAMAN SPECTROSCOPY
H. Richter, L. Ley

To cite this version:
H. Richter, L. Ley. GROWTH OF PLASMA-TRANSPORT MICROCRYSTALLINE SILICON AS STUDIED BY IN-SITU RAMAN SPECTROSCOPY. Journal de Physique Colloques, 1982, 43 (C1), pp.C1-247-C1-251. <10.1051/jphyscol:1982134>. <jpa-00221791>

HAL Id: jpa-00221791
https://hal.archives-ouvertes.fr/jpa-00221791
Submitted on 1 Jan 1982

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
GROWTH OF PLASMA-TRANSPORT MICROCRYSTALLINE SILICON AS STUDIED BY IN-SITU RAMAN SPECTROSCOPY

H. Richter and L. Ley

Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, 7000 Stuttgart 80, F.R.G.

1. Introduction. - In 1980 Iqbal et al. (3) showed that it is possible to deposit crystalline silicon at temperatures as low as 200°C from the gas phase in a plasma transport process. Since then a number of different methods have been developed that give also microcrystalline silicon (μc-Si) with typical grain sizes of 10 nm at deposition temperatures around 300°C such as sputtering (4,5) and glow-discharge decomposition of SiH₄ (6,7,8). This new material combines high conductivity and doping efficiency (9) with a preparation compatible with that of amorphous, hydrogenated silicon (a-Si:H). This fact makes μc-Si a promising material for applications like high conductivity electrodes for a-Si:H solar cells (10).

The physical properties of c-Si such as structure, optical absorption, and elec-
trical conductivity have been investigated intensively (5-11). However, little is known as yet about the details of the growth process that favours crystallization at temperatures several hundred degrees below the crystallization temperature of a-Si (~700°C). In this paper we present the first in-situ studies of the growth of μc-Si films, using first order Raman spectroscopy. This technique provides a fast and convenient method to determine the crystallinity of a Si film. A narrow (3.5 cm⁻¹) line at 520 cm⁻¹ due to the excitation of the q=0 optical phonons is characteristic for c-Si, whereas Raman spectra of a-Si exhibit a broad (50-80 cm⁻¹) hump centered around 480 cm⁻¹. This hump actually reflects the phonon density of states in a-Si (for details see for example (12) and references given there).

We have used the first order Raman-spectra to monitor the relative contributions of a-Si/μc-Si during the growth of the μc-Si films and after removing portions of the films by plasma-etching or sputtering. The temperature of the growing film was deduced from the intensity ratio of the Anti-Stokes/Stokes contributions to the Raman spectrum.

2. Experimental. - In-situ Raman spectra of μc-Si films were obtained in a set-up that combines a conventional Raman spectrometer with our plasma-transport reactor (see fig. 1, for details of the preparation system see ref. (9)). Raman spectra were thus taken at different stages of deposition without exposing the growing film to atmosphere. The deposition temperature \( T_D \) was 350°C except for some of the measurements in the growing film where \( T_D \) was 250°C.

A 100 nm molybdenum film evaporated on parts of a polished silicon (111) surface served as a substrate while the uncovered part of the Si was used for alignment of the optical system. Mo was chosen as a substrate because

1) there is very little interdiffusion between Mo and Si up to 1000°C,
2) Mo and Si do not form eutectics that crystallize below 800°C (13),
3) in the frequency range between 400 and 600 cm⁻¹, Mo has a structureless low scattering background.

The films could also be etched in a pure hydrogen plasma or by Ar ion sputtering (150 μA/cm² at 280 V) at room temperature. The Raman spectra were excited with an Ar laser using 200-400 mW power, focussed with a cylindrical lens on the samples in order to avoid local heating. Between wavelength in the range 457.9 nm to 514.5 nm of the exciting laser, no significant differences in the Raman spectra were found. All spectra shown here are thus taken with the 488 nm laser-line with a resolution of 10 cm⁻¹. The penetration depth for this wavelength is of the order of 100 nm in μc-Si (9).

The intense and highly structured background of visible light emitted by the hydrogen plasma (14) made it necessary to take difference spectra in those cases where the Raman spectrum was measured during film growth. This was achieved by chopping the exciting laser light and by subtracting the "laser off"-counts from the "laser on"-counts immediately in a multichannel analyser.
3. Results and Discussion. - Fig. 2 shows a typical sequence of Raman spectra of a Si film taken at various stages of the deposition. The thickness of the final film was measured with a mechanical thickness gauge to be 0.45 μm. Assuming a constant growth rate of 0.1 nm/s, the thickness of the film corresponding to the spectra in fig. 2 can be estimated. It is obvious from the spectrum taken after 80s, that approximately the first 8 nm of the Si film are purely amorphous. This is to our knowledge the first experimental evidence that μc-Si starts growing amorphous.

During further deposition the crystalline Raman line begins to show up. After about 4000s a final spectrum evolves that does not change with further deposition. The ratio of "crystalline" (at 520 cm⁻¹) versus "amorphous" (at 480 cm⁻¹) Raman intensity, \( I_c/I_a \), is plotted in fig. 3.

![Graph showing Raman spectra](image1)

**Fig. 2**: Raman spectra of silicon films taking after successive deposition. \( t_{dep} \) is the accumulated deposition time. The spectra of films with \( t_{dep} \geq 300s \) are normalized to 1, spectra 160s and 80s are the same scale as spectrum 300s. From the thickness of the final film of 0.45 μm we calculate a growth rate of 0.1 nm/s.

![Graph showing intensity ratio](image2)

**Fig. 3**: Intensity of crystalline versus amorphous Raman line \( I_c/I_a \) versus film thickness.

\( x \) during growth of the film. The thickness is calculated from the deposition time assuming a constant growth rate.

\( 0 \) during \( H_2 \)-plasma-etching of the film.

The thickness of the initial film is estimated from the deposition time and the ratio \( I_c/I_a \). After etching the thickness of the film is estimated from the total Raman intensity.

The saturation value of \( I_c/I_a \) is determined by the bulk ratio of crystallites and amorphous material. It varies with deposition parameters (11).

In order to study whether or not an amorphous layer remains near the substrate after further deposition, we deposited a μc-Si film of approximately 40 nm thickness under the same deposition conditions. When this film was etched under the influence of a hydrogen plasma, we measured the sequence of Raman spectra plotted in fig. 4.
This implies that the ratio $I_c/I_a$ in Fig. 3 represents the fraction of crystalline material in the silicon film. The reduction in Raman intensity with etching time indicates that the uc-Si specimen is thinned under the action of the hydrogen plasma. Note, however, that the etch rate is two to three times that of the deposition rate despite the fact that the plasma density is reduced by a factor 0.04 compared to the deposition of Fig. 2. Also and most important the film retains a crystalline component down to the last few nanometers and there is no sign of an increase in the amorphous component as we approach the substrate. In fact, the ratio $I_c/I_a$ remains virtually constant through the etching series as indicated in Fig. 3 by the open circles. In general, our data indicate that the ratio $I_c/I_a$ remains virtually constant with etching, regardless where we start on the deposition curve of Fig. 3.

We can interpret these results in the following way:

(i) The initially amorphous portion of the film crystallizes as the film grows.

(ii) The film is homogeneous at each stage except possibly for the time it takes to grow the first 30 nm which were not investigated ($\approx 300$ sec). This implies that the ratio $I_c/I_a$ in Fig. 3 represents the fraction of crystalline to amorphous material throughout the film at each stage. We can, at present, not decide whether the increase in $I_c/I_a$ reflects an increase in the number of crystallites or in their size. This decision would be in principle possible based on the position and width of the 520 cm$^{-1}$ component of the Raman spectrum (12). However, the high sensitivity needed in these experiments prevented the necessary spectral resolution ($\approx 2$ cm$^{-1}$).

We can dismiss thermal crystallization of the initially amorphous 8 nm of the films for the following reasons. The macroscopic temperature of the growing film never exceeded 380°C as measured by a thermocouple attached to the substrate surface. A lowering of the crystallization temperature due to internal stresses for example was not observed. Taking an 8 nm amorphous layer through a series of annealing steps for two minutes at each temperature crystallization set in at 730°C in agreement with the crystallization of thick amorphous films. The two minutes are equal to the time needed to observe the first sign of crystallites in the growing film (compare Fig. 2).

The macroscopic temperature measurement does not exclude a strong local heating in the film. We have therefore studied the film temperature during the growth of uc-Si by measuring the ratio of the Stokes $R_S$ and Anti-Stokes $R_{AS}$ Raman intensity. This ratio $R_S/R_{AS}$ is given by (15)

$$R_S/R_{AS} = C \cdot \exp \left( \frac{h\omega_0}{kT} \right),$$

where $h\omega_0$ is the phonon frequency, $T$ is the absolute temperature, $C$ is determined by absorption coefficients, frequencies, and cross-sections of the Stokes and Anti-Stokes-light. From a measurement of $R_S/R_{AS}$ at a known temperature (here 250°C, while the plasma was off) the preexponential $C$ has been determined. From measure-
merits of $R_S/R_{AS}$ during film growth we obtained a temperature rise of $40 \pm 30^\circ \text{C}$ to $290 \pm 30^\circ \text{C}$ during the deposition process in agreement with the thermocouple measurements. A temperature rise approaching crystallization temperature even in a 10 nm surface layer could be excluded as well from a detailed analysis of the shape and position of spectra.

4. Conclusions. - The results presented here allow the following conclusions to be made about the growth of $\mu$-c-Si from the plasma transport process. The films start to grow initially with no detectable crystallinity up to a thickness of about 8 nm. Further growth proceeds in such a way that microcrystals are formed and the ratio of crystalline to amorphous material increases until a crystallinity is reached that depends on the deposition parameters. The etching experiments show that at each stage the crystallinity of the film is homogeneous including the initially amorphous 8 nm. This requires a crystallization process that is not limited to the growing surface alone. Temperature measurements using Raman techniques during film growth and annealing studies exclude a thermal crystallization process of the amorphous layer. These observations are corroborated by post deposition crystallization of CVD a-Si in a hydrogen plasma at 400°C by Bustarret et al. (1). Crystallites are detected to a depth of at least 500 nm and their size increases with exposure to the plasma up to 10 nm.

There is little doubt, therefore, that a high density hydrogen plasma plays the essential role in these low temperature crystallization phenomena. Veprek et al. (2) suggest that part of the energy released by the recombination of hydrogen atoms at the surface to form $\text{H}_2$ molecules provides the "activation energy" for nucleation and growth of crystallites by non-thermal population of zone boundary phonons. Our results and those of Bustarret et al. require, however, that the energy is transmitted up to 500 nm into the film. It is at present not clear whether such an energy transfer could take place without a thermalization of the phonons that would show up in the Raman spectrum.

5. References.