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Crystallinity of the mixed phase silicon thin films by Raman spectroscopy

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Abstract

Raman spectra of the mixed phase silicon films were studied for a sample with transition from amorphous to fully microcrystalline structure using four excitation wavelengths (325, 514.5, 632.8 and 785 nm). Factor analysis showed the presence of two and only two spectrally independent components in the spectra within the range from 250 to 750 cm^{-1} for all four excitation wavelengths. The 785 nm excitation was found optimal for crystallinity evaluation and by comparison with surface crystallinity obtained by atomic force microscopy, we have estimated the ratio of integrated Raman cross-sections of microcrystalline and amorphous silicon at this wavelength as $y = 0.88 \pm 0.05$.

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Keywords: Silicon; Raman scattering; Chemical vapor deposition; Atomic force and scanning tunneling microscopy; Raman spectroscopy

1. Introduction

The most important characteristic of mixed phase silicon layers, affecting all other film properties, is the crystallinity, i.e., the volume fraction of crystalline phase [1,2]. It is commonly determined by measuring the LO–TO peak of the Raman scattering spectra composed of a broad band centered around 480 cm^{-1}, attributed to the amorphous phase, and of a sharp peak at 520 cm^{-1}, originating from the microcrystalline part of the layer.

The first step for the crystallinity evaluation is a decomposition of the spectra into amorphous and microcrystalline contributions. The most widely used method is a numerical least-squares fitting of the spectra by a sum of three Gaussian or Lorentzian peaks [3,4]. Two peaks centered around 520 and 500 cm^{-1} are used to describe asymmetrical crystalline part of the spectra and the third peak at 480 cm^{-1} is used to represent the contribution of the amorphous fraction. However, the interpretation of the contributions, especially of the middle band located between 495 and 510 cm^{-1}, sometimes called the 'third phase', is not clear. The second frequently used technique is based on the fact that the amorphous part of the spectra is also asymmetrical and so a single Gaussian band can not represent its contribution to the spectra. Smit et al. [5] solved this problem by using Raman spectrum of pure a-Si:H to represent the amorphous contribution of the mixed phase silicon spectrum.

Crystalline volume fraction X_C is then derived from a simple formula firstly published by Tsu et al. [6]

$$X_C = I_c/(I_c + yI_a), \tag{1}$$

where I_c and I_a are the integrated Raman signals from the crystalline and amorphous parts, respectively, and y is the ratio of the integrated Raman cross-sections for

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microcrystalline and amorphous silicon. If the material is strongly absorbing the excitation laser wavelength then y may be expressed as

$$y = I_c\alpha_c / I_a\alpha_a, \tag{2}$$

where α_c and α_a are absorption coefficients of the fully crystalline and fully amorphous layer respectively. Values of y from 1.7 down to 0.8 have been published for 514.5 nm excitation wavelength [6,7]. The ratio y varies with the excitation wavelength thanks to the resonant character of amorphous [8] and microcrystalline [9] LO–TO band. In the case of nanocrystalline silicon (porous silicon, Si nanoparticles or nanowires) with the characteristic size smaller than 15 nm the parameter y depends also on the size [10,11], but this is usually not the case of microcrystalline silicon suitable for photovoltaics.

Mixed phase layers are often non-uniform: the bottom part is usually fully amorphous and then the crystallinity is increasing with the growing thickness. Therefore the depth which is probed by laser light, the so called Raman collection depth (RCD), is critical for the correct interpretation of the Raman spectra. For homogenous material RCD is given by absorption in the material

$$\mathrm{RCD} = 1/2\alpha, \tag{3}$$

where α is absorption coefficient for the excitation wavelength, but the situation may be more complicated in the mixed phase layer with large grains [12].

The assumptions implicit in the crystallinity evaluation described above may influence the results. In this contribution we address them using the following approaches:

(1) We use factor analysis [13] to test what is the number of independent components of the spectra regardless of their spectral form. Namely we have tested whether the so called third phase is necessary for the spectra decomposition.
(2) The crystallinity obtained by spectra decomposition is compared with the crystallinity evaluated independently from atomic force microscopy (AFM) topography images. This comparison is used to estimate the value of y ratio for the selected Raman spectra excitation wavelength.

Factor analysis is a mathematical procedure, which projects the experimental spectra into orthonormal spectral base composed of the so called sub-spectra S_j. We used singular value decomposition (SVD) algorithm for this purpose. Every experimental spectrum E_i may be expressed as

$$E_i(v) = \sum W_i V_{ij} S_j(v), \tag{4}$$

where V_{ij} are elements of a unitary matrix which represents relative contributions of the sub-spectra S_j and singular values W_j are statistical weights of the sub-spectra S_j. The key point is establishing of the minimum number of sub-spectra N sufficient for representing correctly the experimental data. Convenient criterion of good fit seems to be the Cattell scree plot, i.e., the plot of the singular values W_j as a function of the sub-spectra number. Low singular values W_j (usually below 0.5%) identify sub-spectra of white noise signal level [13].

2. Experiment

In this study we have used the same silicon layer as at the last conference [12]: the layer with 900 nm thickness prepared by plasma enhanced chemical vapor deposition from 1:33 mixture of silane in hydrogen. The temperature during the deposition was kept at 100 °C due to the 200 μm thick polyethylene terephthalate (PET) foil used as a substrate. The deposition plasma was magnetized by a 4 mm wide permanent magnet placed under the substrate [14,15] with its axis perpendicular to the substrate, which influenced the nucleation density and changed the crystallinity of the layer depending on the distance from the edge of the magnet, see Fig. 1. In this way we obtained a range of structures from amorphous to fully microcrystalline deposited at otherwise identical conditions.

Microscopically resolved Raman scattering spectra were measured in back scattering setup at predefined locations on the sample with 4 different excitation wavelengths: 325 nm HeCd laser or 785 nm diode laser with line shape focus (3 × 20 μm) and laser power 0.3 mW and 5 mW on the sample, respectively, measured by Renishaw InVia REFLEX, and 514.5 nm Ar^+ laser or 632.8 nm HeNe laser with spot diameter 10 μm (∼1 mW) measured by Renishaw RM1000 micro-Raman.

Atomic force microscopy was used for detailed surface analysis and evaluation of the surface crystallinity. Topo-

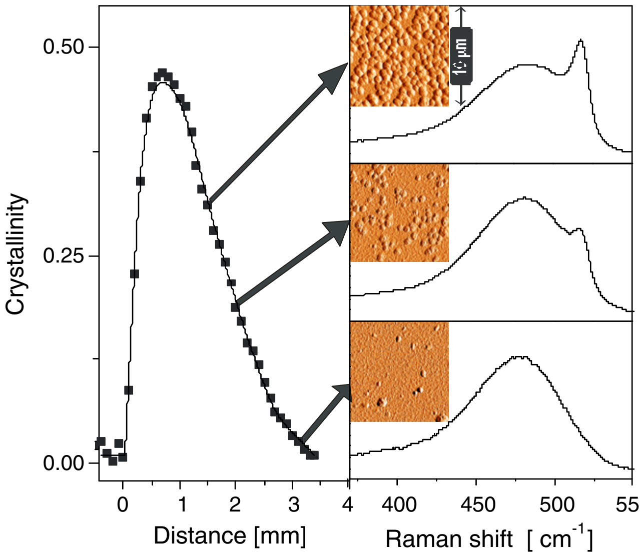

Fig. 1. Transition across the microcrystalline/amorphous boundary on the surface of the sample grown above the permanent magnet. The left graph shows the crystallinity X_C as a function of the distance from the magnet edge. Values of X_C were evaluated from the Raman spectra such as shown at three different positions in the right together with the corresponding AFM surface structures.