Investigation of deposition conditions on the structural properties of μc-Si:H

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Abstract. This article is concerned with Raman study of μc-Si:H obtained by PECVD under different deposition conditions. The analysis of crystal fracture and bonded hydrogen content in the layer was carried out. It is shown that as the amorphous phase increases, the content of Si-H bonds prevails. Optimal conditions for deposition of microcrystalline silicon with a low content of hydrogen bonds were defined.

1. Introduction

Today microcrystalline silicon finds application in the field of solar cells, thin-film transistors and optical sensors. One of the promising ways of using microcrystalline silicon is a creation of semiconductor superlattices with quantum-size effect of ultrathin films [1]. However, when such structures are fabricated by plasma-chemical deposition (PECVD), the specific features appears concerning the structure of microcrystalline silicon. High degrees of dilution of silane (SiH₄) in hydrogen are used to obtain microcrystalline silicon, instead of amorphous silicon. This leads to the fact that the concentration of atomic and molecular hydrogen in the resulting layer is quite high. During the formation of subsequent layers the weakly bound hydrogen under the influence of temperature forms a molecule and comes out from the layer. In the formation of multilayer structures, this process of effusion can lead to delamination and destruction of the deposited layers and the formation of cavities in a multilayer structure [2]. The actual problem is production of μc-Si:H with a low content of excess hydrogen in the layer. Thus the estimation of the influence of the deposition conditions on the structural properties and concentration of hydrogen in the μc-Si:H layer is an important issue.

2. Experimental

The layers of microcrystalline silicon were obtained by plasma-enhanced chemical vapor deposition at the temperature of 380°C on fused silica substrates. During deposition process the dilution of silane in hydrogen varied in the range of 1% to 4% and the power of capacitively-coupled 13.56MHz RF plasma varied from 20W (44 mW/cm²) to 60W (132 mW/cm²) respectively. The structural properties and concentration of bound hydrogen in the μc-Si:H layers were studied by Raman spectroscopy in the range of 400–550 cm⁻¹. The radiation intensity of the Raman spectrometer at a wavelength of 532 nm was adjusted in such a way that there was no local heating of the silicon layer. Maximum intensity of the latitude optical mode (LO) of crystalline silicon in the Raman spectrum corresponds to 520 cm⁻¹, whereas for amorphous silicon it is 480 cm⁻¹. The crystallinity fraction (Xc) of the obtained layers was estimated from the formula in accordance with [3],

\[ X_c = \frac{I_{520}}{I_{520} + I_{480}} \]
where $I_{480}$ is the Raman intensity of the maximum at a wavenumber of 480 cm$^{-1}$, $I_{520}$ is the intensity of the LO peak at 520 cm$^{-1}$. The intensity of each maximum was obtained by deconvolution of the original spectrum. It should be noted that the LO peak for microcrystalline silicon could be shifted to the lower wavenumbers relative to the value for crystalline silicon at 520 cm$^{-1}$ due to decreasing of crystallite size lower 100 Å [4]. The presence of bonded hydrogen in microcrystalline silicon was indicated by peaks in the Raman spectrum at 2000 cm$^{-1}$ and 2100 cm$^{-1}$ corresponding to the resonance frequency of Si-H and Si-H$_2$ bonds [5]. Content of n(Si-H) and n(Si-H$_2$) bonds in the layer can be roughly estimated using formulas:

$$n(Si - H) = \frac{I_{2000}}{I_{520} + I_{480}}$$

(2)

$$n(Si - H_2) = \frac{I_{2100}}{I_{520} + I_{480}}$$

(3)

where $I_{2000}$ is the Raman intensity of the maximum at a wavenumber of 2000 cm$^{-1}$, $I_{2100}$ is the intensity of the maximum at 2100 cm$^{-1}$.

3. Results

Silicon deposition processes were performed with variations of the pressure, plasma power and the degree of SiH$_4$ dilution in hydrogen. Deposition time in all processes was set to 20 min. Resulting Raman intensity strictly depends from focusing of incident laser which was manually adjusted and should not be compared from sample to sample. But the relative intensity of the maxima on each spectrum can be considered as a reliable indicator of the material properties. For clarity, the intensity of the Raman spectrum in the range of 1900 - 2200 on all graphs was increased by a factor of 10.

3.1 Deposition pressure

The variation in value of deposition pressure was carried out at a constant power of 60 W and a dilution degree of 2%. Raman spectra (figure 1) demonstrate that at deposition pressure above 500 mTorr the saturation of crystal line fraction appears, which is indicated by a more pronounced peak at 520 cm$^{-1}$.

Figure 1. Raman spectra of microcrystalline silicon obtained at various pressures (a). Hydrogen content and crystal fracture in dependence of deposition pressure (b).

Total concentration of hydrogen slightly varies with increasing pressure and has a minimum at 500 mTorr. The intensity of the maximum at 2100 cm$^{-1}$ is higher compared to that at 2000 cm$^{-1}$ in μc-Si:H layers with higher crystallinity.

3.2 Plasma RF power

Raman study of dependence of the plasma RF power on the structure of layers and hydrogen content was carried out at constant pressure of 700 mTorr and SiH$_4$/H$_2$ dilution of 2% (figure 2).
We can note a strict dependence of the crystalline fraction of the layer on all three variable parameters. The increase in pressure and deposition power leads to an increase of crystalline fraction. It can be said with certainty that the crystal fraction increases with the power of the plasma, which is confirmed by a decrease in intensity of 480 cm$^{-1}$. Saturation of the influence of power on the crystal fraction occurs at 40 W (88 mW/cm$^2$). It can also be noted that decrease of amorphous phase fraction indicated by Raman intensity drop at 480 cm$^{-1}$ is followed by rise of Si-H$_2$ bond concentration. The increase of Si-H$_2$ bond concentration with fraction of µc-Si:H is associated with a fact that Si-H$_2$ bonds are mostly located at the µc-Si grain boundaries.

### 3.3 SiH$_4$/H$_2$ dilution

The layers were obtained at different SiH$_4$/H$_2$ dilution with constant RF power of 20 W and constant pressure of 700 mTorr (figure 3).

The crystalline fraction strictly depends on the concentration of SiH$_4$ during the deposition process and increases with higher dilution. At SiH$_4$ concentration of 4% or more, the layer is completely amorphous, as indicated by the absence of a maximum at 520 cm$^{-1}$. Increase of crystalline fraction is clearly followed by decrease of the bonded hydrogen content.

### 4. Conclusions

We can note a strict dependence of the crystalline fraction of the layer on all three variable parameters. The increase in pressure and deposition power leads to an increase of crystalline fraction. It can be
explained in terms of higher ion energy of Si, and Si-H, Si-H₂ radicals for increased specific power of RF plasma discharge. By varying the SiH₄ concentration from 1% to 4%, the structure of the layer changes from microcrystalline to completely amorphous followed by increase of the hydrogen content. The increase in pressure does not give an explicit dependence of the hydrogen content in the layer; however, we can note a higher content of Si-H₂ bonds at higher pressures. Thus, the optimum parameters for the production of microcrystalline silicon by PECVD with a low content of bonded hydrogen are increase values of pressure and RF power with a lower concentration of SiH₄ in hydrogen.

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