Tailoring the Structure of Low-Temperature-Deposited Microcrystalline Silicon Films by Biasing the Substrate

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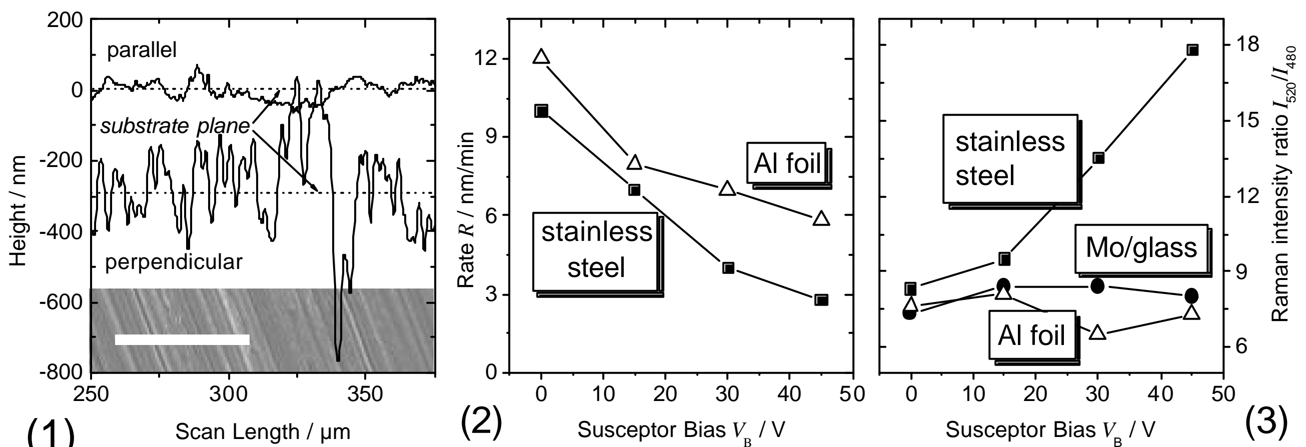
ABSTRACT

Biasing the substrate during deposition and the substrate's surface morphology may both have major effects on the structural properties of thin films. We present the results of structural investigations (Raman and FTIR spectroscopy, XRD, SAXS) of thin silicon films that were prepared at low temperatures by electron-cyclotron resonance (ECR) chemical-vapor deposition. The effect of substrate bias during the deposition was investigated for positive DC susceptor biases V_B ranging from 0 to 45 V. For stainless steel substrates with an artificially enlarged surface roughness (smart substrates), an increase of the crystallinity could be observed with Raman spectroscopy. Films prepared under a susceptor bias of +15 V exhibited a texture inversion of preferential (220)- to (111)- oriented grains, which was accompanied by an increase in grain size from 18 to 42 nm. Small-angle X-ray scattering (SAXS) revealed the films as deposited on Al foil to exhibit significant free volume fractions (microvoids). The ability of tailoring the structure of thin Si films by applying a bias is discussed in terms of controlling the energy and intensity of ion flux to the surface of the growing film. This can efficiently be achieved in an ECR system, where the mean free path of gas particles exceeds the thickness of the plasma sheath.

INTRODUCTION

The electronic properties of poly- and microcrystalline thin Si films are significantly affected by structural features and concentrations of distinct lattice faults. The dimensions of silicon grains in microcrystalline silicon, μc-Si, films are typically of the order of some 10 nm which has to be improved in order to arrive at the required values of charge carrier mobilities for electronic applications. On the other hand, for large-area applications the deposition temperature should not exceed a limit of about 800 K, above which glass or other inexpensive substrates are harmed or electronically deleterious impurities are introduced via interdiffusion. For film growth, the crucial physical quantity is the surface diffusion coefficient of the film-forming species, which should preferably attain a higher value than allowed for by the deposition temperature. Within plasma-assisted thin-film technology, use is often being made of a bias voltage that is applied to the susceptor. By application of this technique ions impinge on the film surface with a kinetic energy of some eV, causing a significant increase of effective temperature due to their thermalization. Advantageously, the effect is combined with an improved compactness of the prepared layer. For physical vapor deposition (PVD) processes, a DC bias that is subjected to the substrates is always negative. A standard process for the low-temperature deposition of thin Si films is plasma-enhanced chemical vapor deposition (PECVD), with the electron-cyclotron resonance ECR PECVD as one of the currently studied options. Also for this technique deposition experiments have recently been reported for which the substrates were subjected to a DC bias [1-5]. It was found that for achieving state-of-the-art film properties a positive bias had beneficial effects. In



Figures

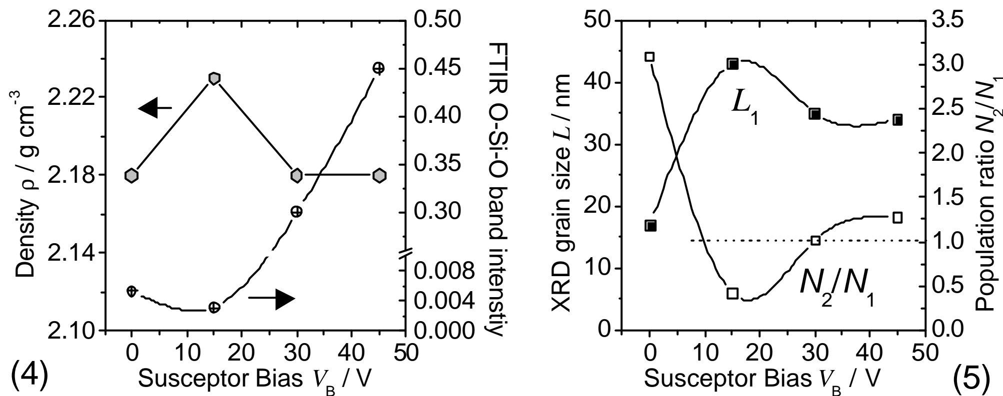
1. *Profilograms of rough stainless steel substrates as measured parallel and perpendicular to the streaking prior to deposition. The inset was obtained by SEM (width of white bar 3 µm).*
2. *Deposition rates for µc-Si films on Al foil and Mo/glass as a function of substrate bias V_B.*
3. *Raman intensity ratio $Q_R = I_{520}/I_{480}$ for films deposited on different metallic substrates.*

this paper we report on structural investigations of a set of thin Si films on metallic substrates that have been prepared by variation of a DC susceptor bias. It will be shown that the bias effects on the structure were especially significant in films which had been grown on substrates with an enhanced surface roughness.

EXPERIMENTAL

µc-Si films were prepared in an ECR deposition system from SiH_4-H_2 mixtures at a total pressure of 0.93 Pa. Silane and hydrogen flow rates amounted to 4 and 90 sccm, respectively, while the substrate temperature was kept at 600 K. The power of the plasma-exciting microwave was adjusted to 1000 W. These optimized deposition parameters have been identified in a previous factorial analysis campaign [6]. The same parameters were used during the preparation of samples presented in this work, except for the biasing of the susceptor, upon which the substrates were placed, which was set to -15, 0, +15, +30 and +45 V. The surfaces of films deposited at -15 V were found to be damaged, causing peeling of some of them. The depositions were carried out simultaneously upon three different metallic substrates each having a surface of 25×25 mm^2, which were Mo-coated Corning glass (Mo/glass), stainless steel (stst) and 10 µm thin, high purity Al foils for SAXS measurements. Prior to the deposition all substrates were built into a metallic mask to ensure electrical contact between the susceptor and substrate surfaces. Stainless steel substrates were produced by laser-cutting from a larger plate and subsequently subjected to an emery process that caused a pronounced streaking, Fig. 1. Its rms roughness parallel and perpendicular amounted to 28 and 94 nm, while it was 4 nm and direction-independent for Mo/glass.

FTIR and Raman spectra were recorded from the prepared films in reflection mode. Film thickness values d were deduced from the FTIR interference fringes by tentatively inserting the refractive index of bulk Si $n_{Si} = 3.42$. The appropriate deposition rates R for films on Al foil and Mo/glass substrates are displayed as a function of substrate bias in Fig. 2. With increasing susceptor bias a continuous slow down of R was found, the slope of rate decrease being approximately -0.14 nm/min per V. Raman spectra were recorded for all three series of samples by exciting with the HeNe laser line (632.8 nm).



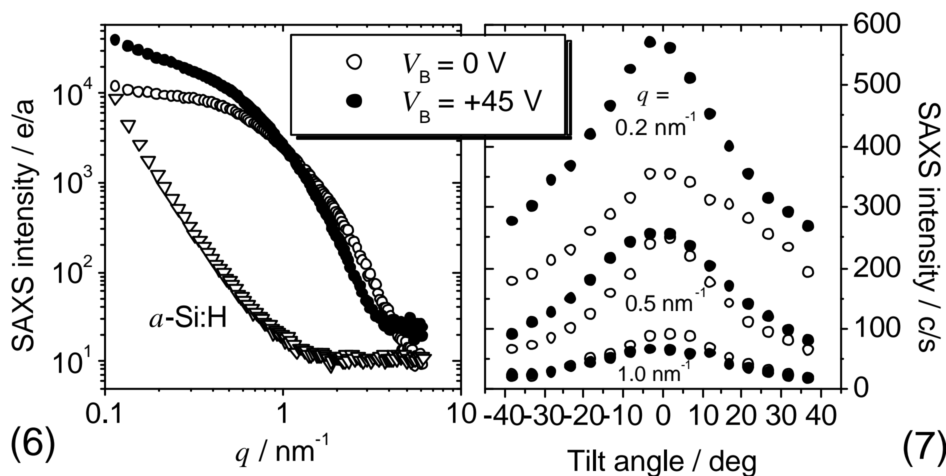
Figures

4. *Flotation denstiy* $\mathbf{r}_{fl}$ *of μc-Si/Al foil (left scale) and integrated Si-O-Si FTIR signal at 1070 cm^{-1} normalized with respect to film thickness d (right scale).*
5. *XRD average grain size* L_1 *as determined from (111) Bragg reflections and concentration ratio* N_2/N_1 *of (220)- over (111)-oriented grains of μc-Si films on stainless steel.*

The typical Raman spectra of μc-Si were obtained exhibiting the *c*-Si LO/TO peak at about 520 cm^{-1} with an asymmetrical broadening and a non-negligible spectral weight at 480 cm^{-1}, where pure *a*-Si would peak. Small Si grains or amorphous fractions within the film may likewise account for a residual intensity at 480 cm^{-1}. The ratio of Raman intensities $Q_R = I_{520}/I_{480}$ is often used as a measure for the degree of crystallinity. The maximum value as obtained in a deposition campaign aiming at the improvement of crystallinity amounted to $Q_R = 8.4$ [6]. Fig. 3 shows Q_R as a function of susceptor bias V_B for μc-Si films deposited on different metallic substrates. A striking increase of Q_R can be realized for films on surface-rough stst substrates whereas, in contrast, Q_R remains essentially constant for depositions on smooth metallic substrates. For +45 V and stst substrates the crystallinity parameter Q_R attained a value of 17.7, which is the largest Q_R ever obtained for a μc-Si film prepared in the ECR system. We consider the increase to be caused by the special surface structure of stst substrates, since it was not observed for μc-Si depositions on smooth metallic substrates.

In addition to this first significant influence of susceptor bias on thin-film structure, a second effect was manifest around $V_B = +15$ V. Fig. 4 displays the density of μc-Si/Al samples that was determined by the flotation method. All films show the same value of $\rho = 2.18$ g/cm^3 except for the sample prepared at 15 V that exhibited an increased density of 2.23 g/cm^3. Moreover, the degree of oxygen contamination of the films has been included in the plot. These values have been obtained by integration of the FTIR band at around 1070 cm^{-1}, where Si-O-Si asymmetric-bond-stretching vibrations in a SiO_x matrix would absorb [7, 8]. We understand the occurrence of this IR band from the *in-situ* and *ex-situ* contamination of samples by oxygen and consider its strength as a measure for microvoids contained in the films. The signal is the smallest for the sample prepared at $V_B = +15$ V. From both results it is concluded that the most compact films are prepared with a DC susceptor bias of 15 V.

Remarkable structural properties of films as deposited at +15 V were also observed by X-ray diffraction in θ–2θ geometry. In general, the growth of μc-Si films prepared within the relevant temperature range with a high degree of crystallinity and larger grains is associated with a preferred orientation of grains exhibiting (220) lattice planes parallel to the substrate plane. The concentration or average number N_2 of such grains within the film competes with N_1 grains of (111)-orientation [9]. The ratio of both, N_2/N_1 may, therefore, serve as a measure how well the (220) texture is developed.



Figures
6. SAXS patterns of μc-Si films on Al foil deposited at V_B = 0 and +45 V. A void-free (f £ 0.01 vol%) a-Si:H sample is shown for comparison.
7. Effect of tilt angle variation on SAXS intensity for fixed q values.

This ratio is shown in Fig. 5 as a function of susceptor bias for μc-Si films on stst substrates. There is also given the average grain size L_1 of (111)-oriented grains in direction of the substrate normal which was derived from the broadening of Bragg reflections. It can be seen that the usual (220) texture is observed for an unbiased substrate, $V_B = 0$. However, at $V_B = +15$ V a texture inversion occurs, i.e. more (111)- than (220)-oriented grains are formed. Simultaneously, the average grain size L_1 increases from 18 to 43 nm. For higher V_B values the texture inversion vanishes and a near-random orientation distribution is observed. Also the average grain sizes decrease again. These effects were not observed for μc-Si films deposited on smooth Mo/glass substrates.

Another most relevant variable regarding the characterization of polycrystalline films is their porosity and free volume fraction, which could effectively be investigated by small-angle X-ray scattering (SAXS). A description of how SAXS signals can be interpreted is given in Ref. [10]. The SAXS patterns of two films prepared at 0 and +45 V are given in Fig. 6 as a function of the momentum transfer vector's magnitude $q = (4\pi/\lambda)\sin\theta$, with 2θ being the scattering angle and λ the CuKα wavelength (154 pm). The films that were prepared at other susceptor biases yielded comparable SAXS patterns and we will therefore restrict the presentation to these two data sets. Also included in the figure is the SAXS pattern of a highly compact PECVD *a*-Si:H sample that contained a vanishing free volume ($\leq$ 0.01 vol%). The measured scattering intensities of μc-Si films are much stronger, indicating a significant free volume fraction.

Data analysis was performed by numerical regression to three different SAXS contributions [10]. We were mainly interested in the component I_N that accounts for the scattering from nanostructural features and the integrated parameter, Q_N. This quantity can be used to estimate a volume fraction of voids, f, assuming this is the origin of SAXS. Alternatively, this intensity may indicate a low-density residual amorphous phase containing large concentrations of hydrogen. It is known from our previous morphological investigations that an amorphous silicon phase may be formed during the initial growth of some 10 nm of film thickness [9, 11]. Hydrogen that is incorporated into subsequently formed microcrystalline parts of the film will primarily be localized on the surfaces of crystalline grains or in grain boundaries. If we assume Q_N to be solely due to the free volume formed by microvoids, f is found to range from 6.7 to 10.7 %. This large value, however, appears unreasonable in view of the flotation densities in Fig. 4, which demonstrate density deficiencies of less than 6.4 % compared to *c*-Si. This discrepancy can be due to anisotropic SAXS. Fig. 7 shows the effect of tilting the two samples at various fixed q values (see ref. 10). The drop in intensity is consistent with elongated scattering objects

oriented with their long axis along the growth direction. We consider this property of microvoids to be in accordance with the columnar growth of the silicon phase that has been observed for depositions on smooth metallic substrates for both $V_B = 0$ V [6] and $V_B > 0$ V [5]. The tilting effect also means that the free volume fractions – derived from Q_N at 0° tilt angle – are overestimated. Based on the drop in intensity shown in Fig. 7, it can be estimated that the actual f values will be about a factor of two smaller. We finally conclude that SAXS measurements indicate that the free volume fraction in the films is maximally in the 3 - 6 % range.

DISCUSSION

It may certainly be expected that more experiments are needed for a thorough understanding of the presented effects. Some aspects, however, may be understood by comparison with the known mechanisms of ECR CVD and conventional PECVD. The total pressure during PECVD generally exceeds that in ECR by 1-2 orders of magnitude and the mean free path of gas molecules in PECVD will accordingly be much smaller than in ECR, the latter of which is found in the cm range. This difference causes the energy distribution function of ions surmounting the plasma sheath and impinging onto the substrate to become narrower in ECR than in PECVD. The ion energy distribution (IED) is centered within a few eV (FWHM) around the plasma potential V_P in ECR [12], while it typically extends from 0 to V_P in PECVD [13]. It is concluded that the V_B variation is associated with an IED tuning. Firstly, the center-of-mass is shifted to lower energies, although the ion energy ($V_P – V_B$) never vanishes, since the V_B increase recursively enhances V_P [1]. Secondly, the ion flux density arriving at the substrate is decreased [14].

In order to understand the presented results we recently argued that two phenomena should be distinguished [5]. The first effect is related to the steady increase of the Raman intensity ratio Q_R as observed on stst substrates. It was pointed out that the top-layers of the growing film will experience an increase of the effective temperature, which can be understood from a net current increase of electrons to the substrate as already observed [2]. Further, in a recent investigation Hamers *et al.* determined the contribution of ions to the growth of thin Si films in PECVD [15]. According to this work the ions can contribute up to 70% to the deposited µc-Si film, while the remaining fraction is formed from the incorporation of radicals. It remained unanswered whether the ions act via direct incorporation of silicon atoms or through the creation of growth sites. We expect the main characteristics of plasma chemistry in ECR and PECVD to operate by comparable principles and, therefore assume that during the growth of µc-Si by ECR a significant fraction of the film is formed by an ionic contribution. The V_B increase will accordingly be associated with a decrease of energy and flux density of ions arriving on the substrate, while the radicals to a first approximation will remain unaffected. The film growth will then become dominated by the radical contribution at the expense of the ionic one. This conclusion is in accordance with the experimental results: (i) the decrease in deposition rate R is understood from the reduction of the ionic fraction of film-forming species, and (ii) it was shown by SEM that the surface morphology of µc-Si on stst substrates with increasing V_B resembles closely to that of hot-wire-deposited films [5], in which case the film is solely grown from radicals [15]. The increasing Raman intensity ratio Q_R is interpreted to be due to an enhanced surface temperature of the growing film and a relative decline of ionic species for the film-forming processes.

The second effect of bias variation upon the structure of µc-Si films refers to the compactness, texture inversion and increase in grain size observed for $V_B = +15$ V. These effects may originate from the IED-shaping influence of V_B upon the ionic contribution of film growth. We conjecture that the IED's center-of-mass is situated at or in the vicinity of a distinct energy which is favorable for µc-Si

growth. Additionally, the texture inversion was only observed for substrates with enhanced surface roughness. In this case the first few 100 nm of film growth will follow the rules of oblique deposition, where next to the known random component of surface diffusion a directed component also has to be considered [16]. We have suggested that the combination of IED tuning and ion-assisted directed surface diffusion should account for the inversion from a (220)- to a (111)-preferred orientation [5].

CONCLUSIONS

We have shown that the application of a susceptor bias during the deposition of μc-Si films on metallic substrates by ECR CVD may induce strong variations of structural properties. Especially interesting effects were found for stainless steel substrates with a pronounced surface roughness. The special shape of the IED in ECR appears of central importance to account for the observed effects. The increase of the Raman intensity ratio I_{520}/I_{480} is understood from an increase of effective temperature in the top film layers in combination with a decline of the ionic contribution to film growth. SAXS and flotation density measurements indicate a noticeable void content in the 3-6 % range. The texture inversion for $V_B = +15$ V is suggested to be due to an ion-assisted directed surface diffusion. Further studies on the effect of susceptor bias during ECR deposition should enable the preparation of μc-Si films with improved grain sizes and crystallinity.

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