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Crystallinity of Thin Silicon Films Deposited at Low Temperatures: Combined Effect of Biasing and Structuring the Substrate

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The improvement of crystallinity of thin silicon films by (i) controlling the ion flux to the substrate and (ii) structuring the substrate surface is demonstrated. Films were deposited by electron-cyclotron resonance chemical-vapor deposition (ECR CVD) at 600 K on grooved substrates that were located on a dc-biased susceptor. The degree of crystallinity as determined by Raman spectroscopy and electron microscopy improved with increasing susceptor bias V_S, which is explained in terms of the local heating of the film surface during initial growth. For $V_S = 15$ V a pronounced increase of grain size was observed by X-ray diffraction that is accompanied by a texture inversion from (110)- to (111)-preferred orientation. The effect is discussed in terms of an ion-assisted reaction step on the surface of the growing film.

KEYWORDS: thin-film structure and growth, electron-cyclotron resonance chemical-vapor deposition, substrate biasing, crystallinity of polycrystalline semiconductors

1. Introduction

The preparation of thin silicon films with a high degree of crystallinity at temperatures substantially lower than 850 K still remains a challenge, the mastering of which would be of great interest for applications in microelectronics and photovoltaics. A temperature T of 850 K accounts for half the melting temperature of Si, $T_M = 1687$ K,[1] that is, a homologous temperature T/T_M of about 1/2. Zone models that were developed for the description of metal film growth,[2,3] predict nonepitaxial films prepared at such low T/T_M values to consist of nanometer-sized crystallites or even amorphous domains. This was found to be in accordance with the results obtained for thin Si films. Minority-carrier lifetimes in such fine-grained material would lie in the 10^{-11} s range, while the mentioned applications necessitate higher values, as usually measured for larger grained material.[4] In this study the combined effect of (i) biasing the substrate and (ii) structuring the substrate surface on the crystallinity and morphology of thin Si films as prepared by electron-cyclotron resonance chemical-vapor deposition (ECR CVD) at 600 K will be demonstrated. The significance of controlling the ion flux to the substrate by dc-biasing the susceptor during the ECR deposition process has already been realized for polycrystalline material[5] and for the homoepitaxial growth of Si.[6,7] These studies confirmed the significant contributions of ionic species to the growth process. Kondo *et al*. speculated that the role of ions is to destroy or change the surface hydrogen coverage.[8] It will be shown here that a suitable surface morphology of the substrate (smart substrate) can influence the growth process and thereby enhance the grain size and crystallinity of thin silicon films.

2. Sample Preparation

Samples were prepared from silane-hydrogen mixtures in an ECR CVD system as described in detail elsewhere.[9,10] The total pressure was 0.93 Pa, while the gas flow rates were 4 and 90 sccm for SiH_4 and H_2, respectively. $1'' \times 1''$ sheets of stainless steel (stst) and Mo-coated Corning glass (Mo) were used as substrates, and were both integrated into a metallic mask system during deposition to adjust the susceptor bias V_S to the substrate surfaces. Deposition times of 180 min were applied for the runs with dc biases of $V_S = 0$, 15, and 30 V. Since the rate decreased significantly with increasing bias, 240 min were used for the deposition at 45 V. The thin-film thicknesses ranged from 650 nm to 1.98 μm. The Mo coating on Corning glasses was prepared by sputtering in an Ar atmosphere. Stainless steel substrates were taken from a larger sheet by laser cutting and afterwards deburred by rubbing with emery paper. While Mo substrates were introduced into the ECR system without further cleaning steps, steel substrates were cleaned by a sequence of wet-chemical procedures prior to the deposition. A pronounced surface structure was introduced into the steel substrates by the emery process. Fig. 1(a) displays a scanning electron microscopy (SEM) top view image of the surface, from which a distinct streaking is observed. The surface roughness of these substrates was measured, using a Tencor profiler, parallel and perpendicular to the streaking. Figure 1(b) shows that the grooves introduced by rubbing became as deep as some 100 nm. The rms roughness values were 28 and 94 nm, respectively, when measured parallel and perpendicular to the streaking. In the following sections, the plane of average height will be considered as the substrate plane. The intense roughness caused most surfaces of the growing film to become inclined with respect to this plane. The surfaces of Mo-coated substrates were rather smooth and maintained a direction-independent rms roughness of only 4 nm. They served as a standard from the comparison with which we deduced the effect of the substrate surface roughness on film growth.

3. Structural Investigations

The crystallinity of the prepared Si films was investigated by Raman spectroscopy using a Dilor/ISA LabRAM with an excitation wavelength of 632.8 nm and a resolution of 1 cm^{-1}. The spectra shown in Fig. 2 correspond to Si films on stainless-steel substrates. A variation of the spectral shape is clearly observed with increasing bias V_S. The signal intensity

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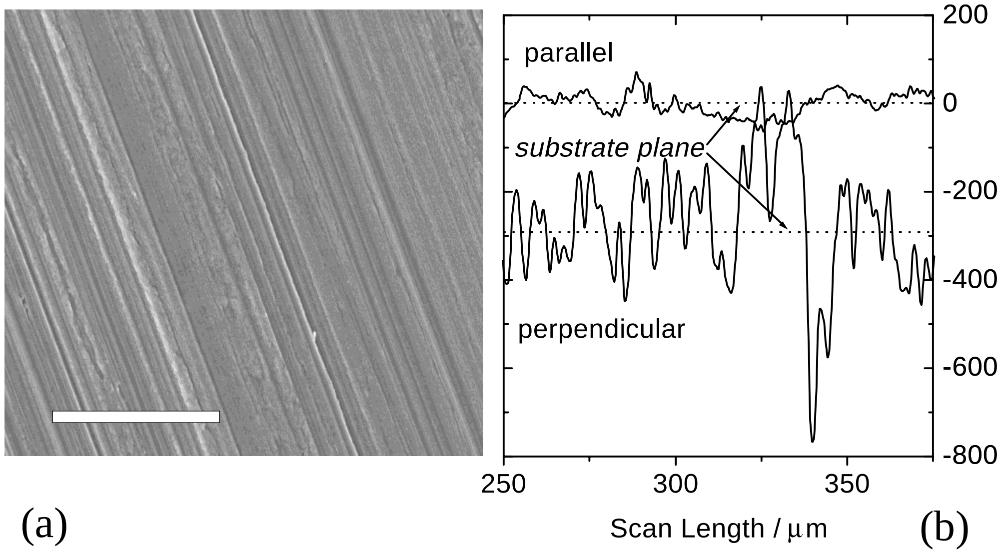

Fig. 1. (a) SEM micrograph of uncoated surface of stainless-steel substrate. The width of the bar is 3 μm. (b) Profilometer recordings of the substrate surface parallel and perpendicular to the streaking. The relative height shift is arbitrary.

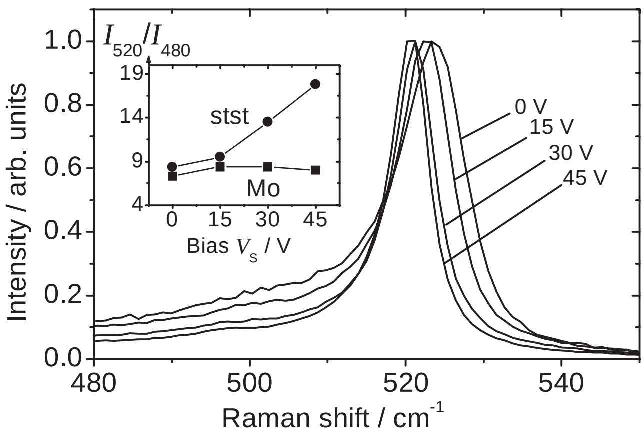

Fig. 2. Normalized Raman spectra of thin silicon films deposited on stainless-steel substrates under varying susceptor bias V_S. The inset shows the Raman intensity ratio I_{520}/I_{480} as a function of V_S for films deposited on both types of substrate.

at 480 cm^{-1} decreases with increasing V_S, which accounts for a reduction of amorphous or any other disordered domains within the samples. Also, the FWHM of the crystalline Si LO/TO peak at 520 cm^{-1} decreases with increasing V_S, indicating an increase in either the crystalline fraction or the average grain size. For a susceptor bias of 45 V the FWHM becomes as small as 6.8 cm^{-1}, which should be compared with a value of 3 cm^{-1} obtained for a silicon wafer under the same measurement conditions. In the former unbiased deposition experiments, the FWHM was minimal at about 10–18 cm^{-1}.

The ratio of the maximum Raman intensity close to 520 cm^{-1} to the Raman intensity at 480 cm^{-1}, I_{520}/I_{480}, is generally considered as a figure of merit for the degree of crystallinity. This quantity is shown in the inset of Fig. 2 as a function of susceptor bias. For comparison, the results obtained for the depositions on the Mo-coated glass are also given. While in the latter case I_{520}/I_{480} remains practically constant, it increases to a maximum value of 17.7 for the deposition on stainless steel at a bias of 45 V. Such a large value has never been observed before in thin Si films prepared on a foreign substrate using our ECR CVD system. Thus far, only a maximum value of 8.2 had been achieved during a systematic investigation of the influence of deposition conditions on the structural properties of the prepared films.[9] The value of 17.7, therefore, indicates a sample with a high degree of crystallinity. In addition to the variation of the line shape, the peak maximum shifted from 523.5 to 520.7 cm^{-1}. In general, maximum positions at higher values than that of *c*-Si, 520.7 cm^{-1}, indicate the existence of compressive stress in the film, while smaller values the existence of tensile stress. The shift of the Raman peak shows that the compressive stress in the films on stainless steel decreases with increasing V_S. Regarding the samples as prepared on the Mo-coated glass, the maximum Raman peak positions were all located on the less-than-520.7 cm^{-1} side. They varied at approximately 519.4 cm^{-1} and exhibited no systematic dependency on the substrate bias.

SEM top view images of the surfaces of the four samples as-prepared on stainless steel are shown in Fig. 3. A change in surface morphology is clearly observed with increasing susceptor bias. The surface structure progresses from cauliflower-like protrusions to a more faceted growth. The morphology observed for $V_S = 30$ and 45 V resembles closely those of thin Si films prepared at higher temperatures of 700–800 K by hot-wire CVD.[11] The corresponding images of samples as-prepared on the Mo-coated glass are given for comparison in Fig. 4. In contrast to the films on stainless steels, fracture edges could be prepared from these samples. Micrographs that display both the cross section of the fracture and the sample surface were taken under an inclination angle of 30°. The films are seen to exhibit the typical cauliflower-like morphology of μc-Si films without a striking change with increasing susceptor bias.

X-ray powder diffraction (XRD) in a symmetric θ–2θ geometry was employed for the investigation of the preferred orientation of crystallites and their average size. Samples on stainless steel were oriented with the streaking parallel to the plane of diffraction. Diffractograms of Si (111) and (220) Bragg reflections were recorded using CuKα radiation ($\lambda = 154.06$ pm) and could be fitted well with Lorentzian

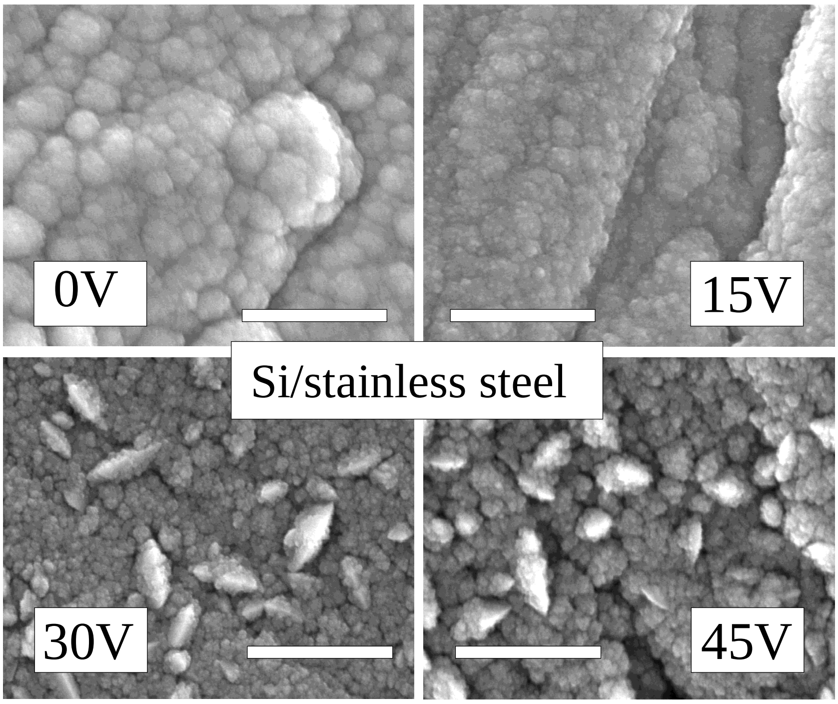

Fig. 3. Top-view SEM micrographs of silicon films deposited on stainless-steel substrates at different susceptor biases V_S (0, 15, 30, and 45 V). The bars are 1 μm long.

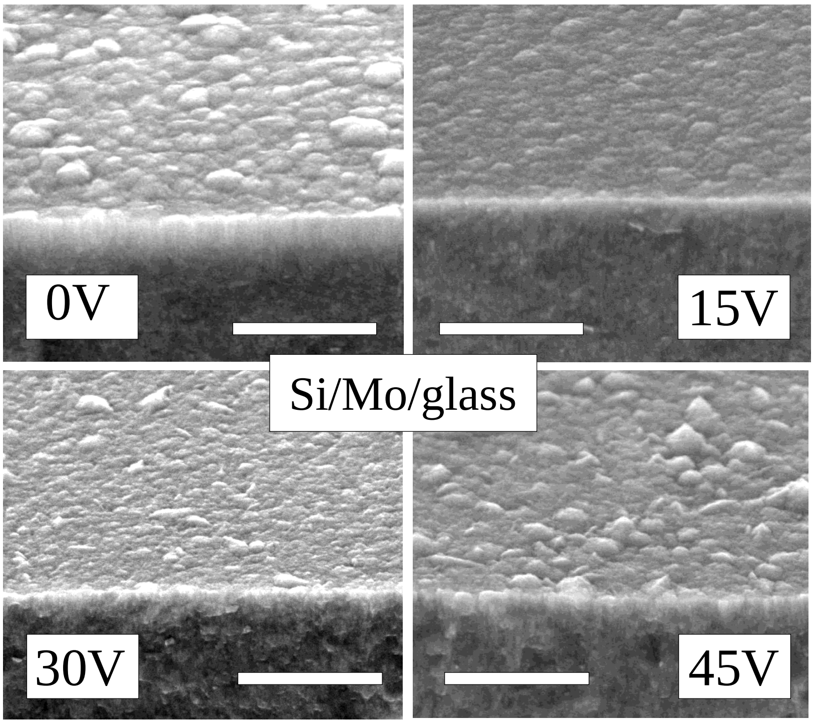

Fig. 4. Side-view SEM micrographs of silicon films deposited on Mo-coated glass substrates at different susceptor biases V_S (0, 15, 30, and 45 V). The bars are 1 μm long.

line shape functions. The average grain size L was evaluated from the peak width B_{hkl} using the Scherrer equation, $L = 0.94\lambda/(B_{hkl} - B_0)\cos\theta$, where θ stands for the Bragg angle of the reflection.[12] The measured peak width B_{hkl} had to be corrected by the instrumental line width function B_0 (2θ) which was determined from a quartz powder standard. Average grain densities, $\bar{N}_1$ and $\bar{N}_2$, exhibiting (111) or (110) crystallographic lattice planes parallel to the substrate plane, were derived from the thickness-corrected integral intensities of (111) and (220) Bragg reflections according to a procedure outlined in ref. 10. Figure 5(a) displays the average grain sizes L_1 and L_2 as functions of susceptor bias for Si depositions on stainless steel, the values of which were found in the 17–43 nm range. L_2 is observed to proceed through a minimum value at 15 V after which it increases. L_1 shows the opposite behavior: it is enhanced from 17 to 43 nm with

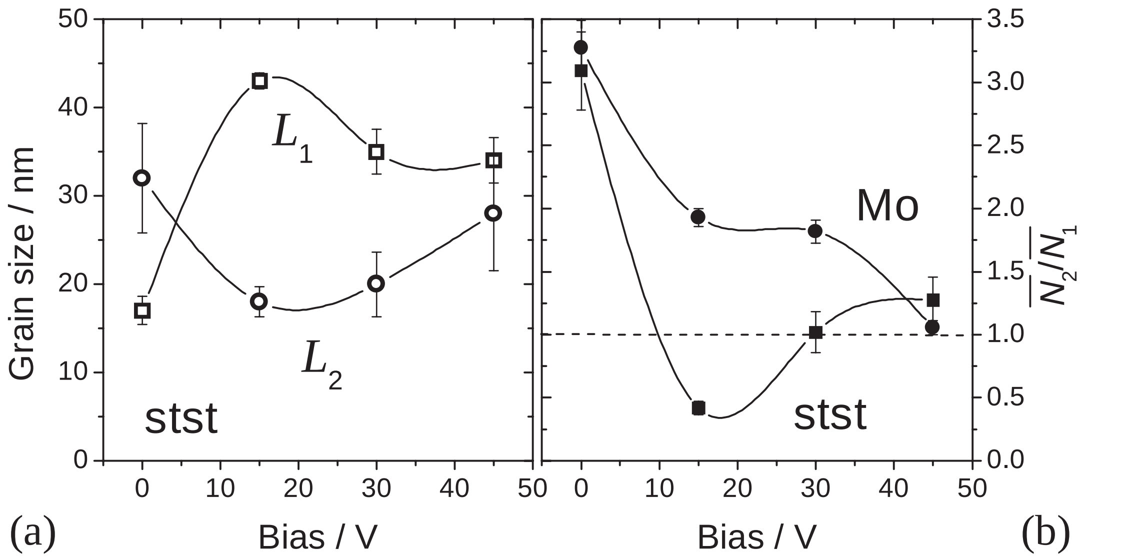

Fig. 5. XRD characterization of Si films on stainless steel (stst) and Mo-coated substrates. (a) Average vertical grain sizes L_1 and L_2 deduced from (111) and (220) Bragg reflections. (b) Average population ratio $\bar{N}_2/\bar{N}_1$ of (110)- over (111)-oriented grains. Connecting lines should only serve as guide to the eyes.

increasing susceptor bias from 0 to 15 V, and decreases to approximately 35 nm for higher V_S values. The pronounced increase in L_1 is associated with a marked change in the texture as evident in Fig. 5(b).

Si films on both substrate types are observed to exhibit a (110) texture when $V_S = 0$ V, i.e. $\bar{N}_2/\bar{N}_1 > 1$. Upon applying a susceptor bias of 15 V, however, the grain population ratio $\bar{N}_2/\bar{N}_1$ switches from 3.1 to 0.42. Thus, under these deposition conditions, more than twice as many grains with (111) lattice planes than those with (110) planes are now oriented parallel to the substrate plane. We conclude that the preferential orientation is inverted from a (110) to a (111) texture for 15 V. This effect is only observed for the samples deposited on stainless-steel substrates. In case of the Mo-coated substrates, the $\bar{N}_2/\bar{N}_1$ ratio monotonically decreases with increasing V_S. For a susceptor bias of 45 V, the texture disappears in both sets of samples and essentially the same average density of (111)- and (110)-oriented grains is obtained. It should be remembered that the measured X-ray intensity is reflected from an extended area of the sample causing a monitoring of crystallographic lattice planes which are oriented perpendicular to the substrate plane normal $\boldsymbol{n}_{\mathrm{plane}}$. On a microscopic scale, the grain orientation with respect to the actual surface normal $\boldsymbol{n}_{\mathrm{surf}}$ may be more relevant regarding the detailed growth process. The situation is schematically shown in Fig. 6, where it can be seen that angle β between both directions may not be zero for many grains. This is another formulation of the fact that the microscopic texture differs form the macroscopic one. Since the angle between [111] and [110] directions is 35.3° for cubic crystals it may even occur that some grains appear to contribute to a {111} texture, while on a microscopic scale they would have to be considered as being preferentially {110} oriented. The most important factor that will be considered in the following discussion is that the orientation distribution function of the film may be influenced by biasing the substrate.

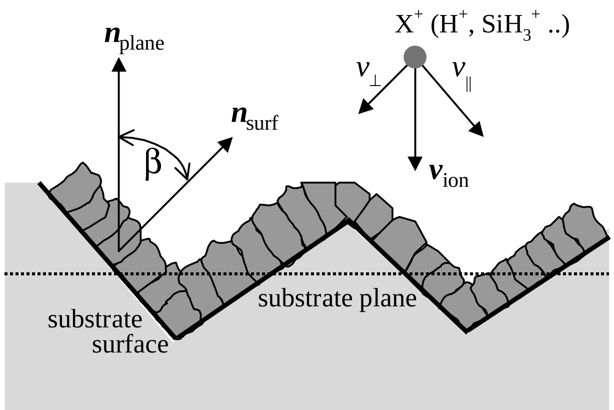

Fig. 6. Schematic of the deposition geometry of Si from SiH_4–H_2 mixtures on a surface-structured substrate. Locally, the substrate surface is inclined with respect to the substrate plane.

4. Discussion

Results of the study provide evidence of the significant effects the susceptor bias and surface structure of the substrate may have on the crystallinity and morphology of thin Si films. Although this first-time presentation of such effects will have to be supplemented by results of further studies in order to develop a thorough under-standing of these interesting phenomena, two major tendencies may already be deduced from these investigations.

The first one is related to the general trend of increasing crystallinity on surface-structured substrates with increasing bias, which is most clearly demonstrated by the inset in Fig. 2 and the changing morphology as revealed by SEM (Fig. 3). Nozawa *et al*. have realized for $V_S = 50$ V that an extra heating of about 20 K was locally introduced into the film's surface, when using a microwave power of 300 W in their experiments.[5] For the depositions presented in this work the microwave power amounted to 1000 W, which may result in an even stronger local heating of the film surface. Moreover, we expect a further-heating mechanism being active during deposition that is caused by the surface structure of the substrates. If energy is introduced from the gas-plasma phase into the substrate by radiation, electron or ion bombardment, a part of this energy is thermally re-emitted into the gas-plasma phase above the substrate in the case of a smooth substrate. For a structured substrate with a large surface area as for example that given in Fig. 1, the main part of the re-emitted thermal radiation strikes the substrate surface again which is simply due to the geometric structure. This re-introduction of heat will continue until the grooves are covered by the growing film. The initial growth will therefore proceed at a higher temperature level than that in the case of a smooth substrate. We argue that for surface-structured substrates, a surplus heating effect is introduced that is mainly limited to the upper-most parts of the growing thin film. This explanation is corroborated by the experimental observation that the film morphology is similar to that of films grown at higher temperatures by hot-wire CVD (see Fig. 3). A further argument stems from the decrease of built-in compression observed by Raman spectroscopy (Fig. 2). The linear thermal expansion coefficient of silicon α_{Si} is about $3 \times 10^{-6}\,K^{-1}$ between 300 and 600 K,[1] which is more than three times smaller than that of stainless steel, $\alpha_{tst} \approx 10^{-5}\,K^{-1}$. Cooling the film-substrate composite after the deposition will accordingly introduce a compressive stress into the film, as is observed for $V_S = 0$. Since the compressive stress becomes smaller with increasing V_S, we conclude that the actual temperature of the growing film is larger than the substrate temperature. This surplus-heating effect accounts for the general trend of increasing crystallinity with increasing susceptor bias.

The second important observation is the marked increase in grain size and the inversion of texture observed for 15 V. To account for this effect, we conjecture that the impinging ions directly influence one of the reaction steps for film growth. The most important film-forming reactions are the surface diffusion of silicon species and the abstraction reaction of hydrogen. It is of interest in this context that Kondo *et al*. demonstrated the control of crystallinity by manipulating the ion bombardment.[8] It is one of the characteristic features of ECR-generated plasmas to operate at such low pressures that the mean free path of gas particles exceeds the thickness of the plasma sheath. Ions travelling towards the substrate will only rarely collide with other particles on their way through the sheath and impinge with a well-defined energy distribution with its maximum energy at the plasma potential V_p. In the case of a perfectly smooth substrate, the ions would strike the substrate surface in the normal direction. For a rough substrate, however, the velocity vector would remain perpendicular only with respect to the substrate plane, but become inclined to most of the surfaces of the growing film. The geometry is schematically presented in Fig. 6. It has been shown by Tae *et al*. that a positive bias applied to the susceptor in an ECR system changes the plasma potential gradient in the zone between the substrate and ECR region from down-hill to up-hill.[13] If the ions are considered to assist in one of the growth reactions, their effect will evidently depend on their kinetic energy and their direction towards the film surface. Firstly, the comparison of Si film growth between smooth and rough substrates indicates that a velocity component of the ions parallel to the film surface causes an enhancement of this reaction. Secondly, the reaction is clearly favored for V_S at approximately 15 V, and suppressed for higher and lower values. The ions' energy must be tuned to an optimum value with respect to a certain activation energy, which is performed by slowing down the ions through a positive susceptor bias. With these considerations, we propose to explain the increased grain size and the strong change in the growth mode at approximately 15 V in terms of an ion assistance of one of the film-growing reactions. The preparation of distinct surface structures should facilitate new experiments for the investigation and potential applications of the interesting effect presented in this work.

5. Conclusions

In conclusion, we have shown that the structure and morphology of thin Si films prepared at low homologous temperatures may be substantially influenced by biasing the substrate in connection with the use of a surface-structured substrate. Significant changes in the degree of crystallinity were observed by Raman spectroscopy with increasing susceptor bias, yielding highly crystalline Si films for $V_S = 45$ V. An increase of grain sizes by a factor of 2.5 was achieved upon changing the susceptor bias from 0 to 15 V. This transition was associated with an inversion of texture from a (110)- to a (111)-preferred orientation. The observed effects are explained in terms of a local heating of the growing film surface and an optimization of the ion energy required to assist one of the film-forming processes. Both phenomena are considered as having unrevealed potential for the preparation of thin Si films with a high degree of crystallinity at low homologous temperatures.

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