Highly ⟨100⟩-oriented growth of polycrystalline silicon films on glass by pulsed magnetron sputtering

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Nominally undoped polycrystalline silicon (poly-Si) thin films were deposited on glass at 450 °C at high deposition rate (>100 nm/min) by pulsed dc magnetron sputtering. The pulse frequency was found to have a significant influence on the preferred grain orientation. The x-ray diffraction pattern exhibits a strong enhancement of the (400) reflex with increasing pulse frequency. The quantitative evaluation reveals that over 90% of the grains are ⟨100⟩ oriented. The observed change in preferred grain orientation in poly-Si films at low temperatures is associated with concurrent ion bombardment of the growing film. [DOI: 10.1116/1.1513634]

I. INTRODUCTION

The low-temperature deposition of crystalline silicon films on foreign substrates has been of vital interest in the past for applications in photovoltaics as well as in displays technology. A particular concern is to achieve reasonably high film growth rates. The charge carrier mobility as a key parameter of the electrical properties is mainly determined by the size and the crystalline perfection of the crystalline grains. It is well known that concurrent ion bombardment of the growing film is a useful approach to realize low-thermal budget thin film growth with striking film properties.[1,2] Recent theoretical[3,4] and experimental studies[5,6] have shown that the growth of crystalline Si films at low homologous temperatures can be stimulated by hyperthermal particle bombardment. In the case of sputter deposition it was shown that low energy (25 eV) high-flux Ar^+ bombardment is beneficial for Si epitaxy at low temperatures.[7,8] In this article we report on structural properties of poly-Si thin films grown by pulsed dc magnetron sputtering[9] on glass at different pulse frequencies. The frequency was found to act as a useful deposition parameter to affect the degree of preferred orientation of Si grains.

II. EXPERIMENT

The sputter deposition system was especially designed for ion-assisted film growth. Thin films were prepared in a high-vacuum loadlock system with a base pressure of 2×10^{-7} mbar. The deposition was performed in an Ar atmosphere with 5N purity at 6×10^{-3} mbar without throttling the pumping speed by use of a massflow-controlling unit (MKS 647B). The magnetron sputter source (AJA Intern. A340) was equipped with a 4 in. circular undoped FZ-Si target and operated in the unbalanced magnetic field mode of type II.[10] The sputtering system was set up in a sputter-down configuration where the target to substrate distance amounted to 75 mm. The plasma generator ENI-RPG 100 was used to pulse the plasma with bipolar asymmetrical dc pulses in the frequency range $f=50$–250 kHz. In our experiments the duty cycle $t_{\mathrm{on}}\cdot f$ was held constant at 0.6. Both the target voltage and the current were recorded simultaneously by a digital oscilloscope to determine the actual and average dissipation power $\langle P\rangle$. We used a biasable and heatable substrate holder from AJA Intern. The substrate temperature, which was calibrated with a commercial wafer process probe (SensArray Corp.), was held constant at 450 °C. The glass substrates (Corning 1737) were partially coated with Mo of 300 nm thickness in order to define the substrate potential to $V_S=0$ V. The investigated films were grown to a thickness of 1.2–1.6 μm at rates in the range $r=41$–251 nm/min by variation of $\langle P\rangle$. Structural film characterization was done by x-ray diffraction (XRD) of 40 kV Cu $K\alpha$ radiation in θ–2θ geometry (URD6) while rotating the samples. For a quantitative evaluation of the XRD results we utilized a formalism[11] that relates the measured integrated reflex intensities I_{hkl} of a Bragg reflection to the relative population C_{hkl} of grains with orientation (hkl). In θ–2θ geometry C_{hkl} represents the relative number of grains with (hkl) surfaces orientated parallel to the substrate surface. In order to derive C_{hkl} from the measured integral reflex intensities the structure factor $|F_T|^2$, the multiplicity m of the reflex, the Lorentz-polarization factor L_P, and absorption factor A have to be taken into account:

$$C_{\mathrm{hkl}}=I_{\mathrm{hkl}}/(F_T\cdot F_T^*\cdot m\cdot L_p\cdot A\cdot K). \tag{1}$$

The absorption factor is especially important in thin films and is calculated as $A=[1-\exp(-2\mu d/\sin\theta)]$ from the Bragg angle θ of the corresponding reflex, the film thickness d, and the absorption coefficient μ (148 cm^{-1} in Si for

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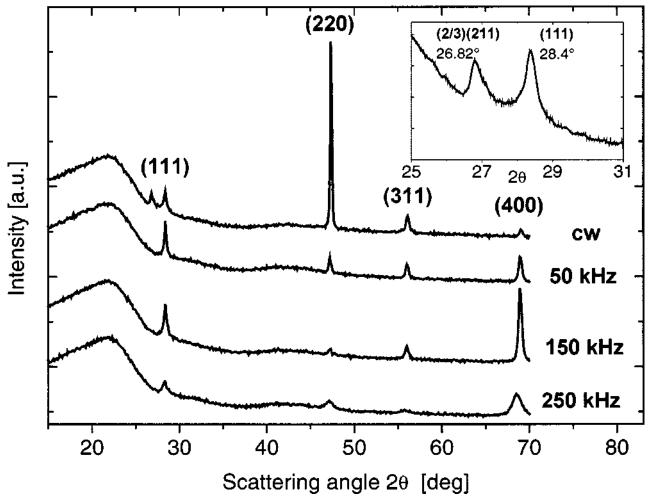

FIG. 1. Raw x-ray diffraction pattern of poly-Si films ($d = 1.2-1.6\ \mu$m) on glass recorded while rotating the samples. The parameter is the plasma excitation frequency. The inset shows the x-ray diffraction pattern in the vicinity of the (111) reflex for the sample grown in cw mode. This data clearly show an additional peak (2/3)(211) at about 26.8°.

Cu $K\alpha$ radiation). The instrument constant K, which is independent of θ, can be neglected in the following, as all samples were analyzed under identical conditions. First, the sum $S = C_{111} + C_{220} + C_{311} + C_{400}$ of all relative populations, for which reflexes were observed in the measured 2θ range, was calculated. By taking the sum over the thickness corrected C_{hkl} one can exclude possible effects due to the variation of the sample thickness.

III. RESULTS AND DISCUSSION

Figure 1 shows the raw XRD diffraction pattern of poly-Si films on glass grown at different pulse frequencies. Independent of the deposition rate for the cw mode the (220) reflex of Si is dominant. This indicates a ⟨110⟩ texture in poly-Si films grown at $f = 0$ kHz, which is typical[12] for sputtered poly-Si films. In contrast, films deposited in the pulsed mode exhibit a strong increase of the (400) reflex indicating a change in preferred grain orientation. Figure 2(a) shows the development of S and film thickness d as a function of the pulse frequency f. A strong increase of S with f is observed up to 150 kHz which cannot be attributed to the small variation in the film thickness. This increase in S denotes that an increasing fraction of grains is oriented in one of the considered directions, i.e., ⟨111⟩, ⟨110⟩, ⟨311⟩, or ⟨100⟩. In fact the dominant part of this oriented growth can mainly be attributed to a large amount of ⟨100⟩ oriented grains as will be shown in the following.

The normalized grain population $N_{\mathrm{hkl}} = C_{\mathrm{hkl}}/S$ gives the fraction of ⟨hkl⟩ oriented grains normalized to all grains entering into S. As the (400) and (220) reflexes represent the first nonforbidden of the (hh0) and (h00) reflexes in the diffraction pattern of silicon, they are indicative for preferential orientation of grains with {110} and {100} lattice planes parallel to the substrate surface. Following this evaluation Fig. 2(b) represents the normalized grain population of each type.

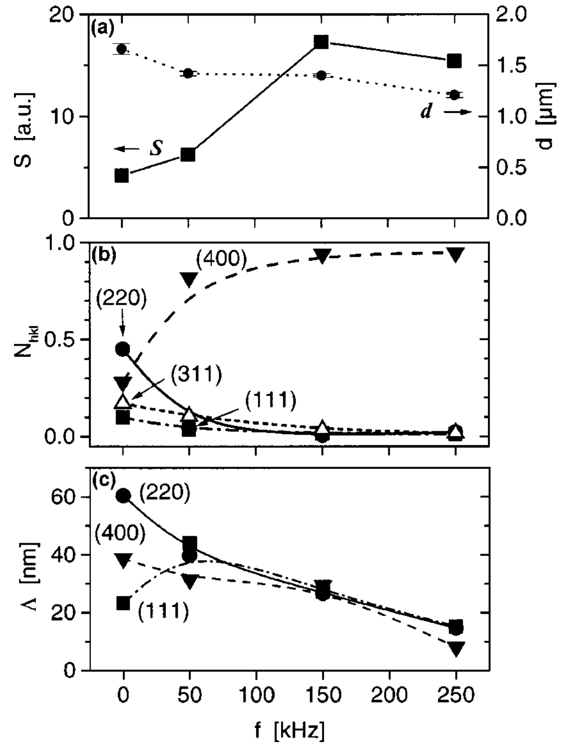

FIG. 2. (a) Sum S of the grain populations C_{hkl} and film thickness d as function of the pulse frequency f. (b) Normalized grain population N_{hkl} as function of the pulse frequency f. A strong ⟨100⟩ preferred grain orientation (fiber texture) appears for $f > 0$. (c) XRD grain size Λ calculated from the full width at half maximum of the (111), (220), and (400) reflexes according to the Scherrer formula.

For the cw mode about half of all grains show a ⟨110⟩ orientation. However, for the pulsed mode we observe in contrast a strong increase of the relative amount of grains with {100} surfaces at the expense of the {110} oriented grains. Already for $f = 50$ kHz about 80% of all grains exhibit a ⟨100⟩ orientation. This behavior is still more pronounced at 150 and 250 kHz where more than 90% of the grains are ⟨100⟩ oriented. These films develop an almost complete fiber texture. It has to be stressed that this strong trend cannot be quantified directly from the raw diffractogram of Fig. 1, but only by evaluating the reflex intensities according to Eq. (1).

Another characteristic difference in the structural properties of poly-Si films deposited in the cw mode and pulsed mode apparently consists in a different defect structure. Figure 1 shows in the inset the 2θ range in the vicinity of the Si (111) reflex of the sample with $f = 0$ kHz. In cw sputtered poly-Si samples with a dominant (220) reflex an additional peak at about 26.8° has always been observed. However, this additional peak (2/3)(211) was not present in samples grown in the pulsed mode. The existence of this reflex was reported before for polycrystalline Si films prepared by chemical vapor deposition[13,14] where it was observable somewhat less pronounced than in the present result. The occurrence of this reflex is suggested to be closely related with a high density of planar faults along {111} planes in the cubic lattice of poly-Si films, and it is considered, therefore, as an indicator for Si twinning lamellas with hcp stacking at the boundaries.[13] Accordingly, the pulsed mode of Si sputtering is concluded to yield a significant reduction of this special kind of lattice faults. Applying the Scherrer formula[15] on our data yields grain sizes Λ in the range of 10–60 nm [Fig. 2(c)]. Assuming that the line broadening is simply due to a grain size effect and neglecting any influence of residual stress in the film as well as corrections with respect to the instrumental line broading, the data in Fig. 2(c) indicate a lower limit of the true values. Cross-sectional transmission electron microscopy analysis of these samples confirmed that, in fact, the actual grain sizes are larger. As a general trend we found a decrease in grain size with increasing pulse frequency. Most surprisingly this is accompanied by an increase of the lattice constant as is deduced from the positions of the diffraction angles.

Our results show that there are significant changes in the poly-Si microstructure with a variation of the pulse operating parameters. Time resolved Langmuir probe investigations indicate two essential differences between the cw and the pulsed mode. With increasing pulse frequency the ion density in the plasma is enhanced. In addition, the plasma potential both during t_{on} and t_{off} was found to be more positive than for the cw excitation. These findings led to the conclusion that in the case of pulsed dc excitation the growth of poly-Si films on grounded substrates is modified by enhanced ion bombardment of the growing film. It is known that preferred ⟨100⟩ orientation of vapor-phase grown poly-Si films requires, in general, substrate temperatures in excess of 600 °C.[16] The observation of this effect at a much lower temperature of 450 °C is supposed to be due to an additional transfer of energy by ion bombardment during film growth since due to the high surface free energy[17] a ⟨100⟩ oriented growth is rather unlikely. Regarding the development of a certain texture under ion bombardment there are different energy-dependent mechanisms under discussion.[18–21] These concern both the nucleation and the following growth kinetics. Under the assumption of a collisionally enhanced adatom mobility[18] a ⟨100⟩ oriented poly-Si thin film growth can be understood as a result of a vertical overgrowth[22] by the fastest growing[23] grains.

IV. CONCLUSIONS

In conclusion this work demonstrates that highly ⟨100⟩ oriented polycrystalline silicon thin films on glass can be grown by pulsed dc magnetron sputtering. In particular, an appropriate choice of the pulse frequency was found to be beneficial to taylor the degree of preferred grain orientation. This finding is an interesting result for crystalline Si thin-film technology in general. Since ⟨100⟩ orientation is most suitable for low-temperature Si homoepitaxy[24] the application of such films as seeding layers for a subsequent epitaxial growth is promising for thin-film photovoltaics.

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