Structural and optical properties of poly-Si thin films obtained by aluminium induced crystallization

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Abstract. The structural properties were studied of poly-Si films prepared by aluminium induced crystallization (AIC) of amorphous Si films (a-Si:H) deposited on glass substrates covered with Al layer. Raman and XRD spectroscopy were used for characterization of their short and long range order, respectively. The UV-reflectance spectra of poly-Si films were measured as well, and their surface morphology was observed by optical microscopy. The dependence was revealed of the structural and optical properties of the poly-Si films obtained on the annealing gas atmosphere and the hydrogen pressure during the deposition of the a-Si:H precursor, together with the correlation between them. The poly-Si films were applied in p-poly-Si/n-ZnO heterostructures; the I-V characteristics of the latter are presented and discussed.

1. Introduction
Recently aluminium induced crystallization (AIC) has attracted attention as a promising technology for low-temperature fabrication of large-area polycrystalline silicon (poly-Si) with grain sizes larger than the thickness of the Si layers [1-6]. It is an economically attractive process for producing poly-Si at a low temperature (<550°C) in a short time starting from small-grained or amorphous Si deposited on a low-cost substrate such as glass or plastic. The preparation of poly-Si films by AIC is based on an annealing of amorphous Si films deposited by different methods. When Si is in contact with certain metals, the a-Si crystallization temperature is drastically reduced. This is due to a change in the Si-Si covalent bonds at the interface Si/metal due to the free electrons from the metallic phase. During the isothermal heat treatment, the semiconductor film is dissolved into the metal film, where it diffuses and precipitates. In spite of the large variety of metals used, Al has found the largest applications in the MIC of a-Si films. The main parameters involved in the AIC, i.e. the annealing temperature, duration and atmosphere, the Al/Si thickness ratio, the interface oxide layer, the layer sequence, the method of Al and Si deposition, etc. have been intensively studied [3-6].

In this review the influence is presented of the annealing atmosphere and the hydrogen concentration in the a-Si:H precursor films on the structural and optical properties of poly-Si films prepared by AIC.

2. Experimental
Poly-Si films were prepared by AIC of the glass/Al/a-Si:H(or a-Si) structures. The precursor Al layers were deposited at a substrate temperature \( T_{\text{Al}} = 300 \, ^\circ\text{C} \) and were kept for 24 hours in air before the
deposition of the a-Si:H (or a-Si) films. Unhydrogenated (a-Si) and hydrogenated (a-Si:H) films were deposited on top of the Al by magnetron sputtering at 130 W rf power, different substrate temperatures, $T_{s}$, and different H$_2$ partial pressures in the gas mixture Ar+H$_2$. The precursor layers, Al and a-Si (or a-Si:H) had equal thickness of about 100-150 nm. The structures prepared were annealed isothermally at different temperatures in the range 480-530°C for different times and in different annealing atmospheres: N$_2$, forming gas (N$_2$+H$_2$) and H$_2$. During the annealing, crystalline silicon grains were formed in the bottom layer, while Al atoms moved to the top surface, which resulted in a layer exchange. After annealing, the aluminium was removed from the surface of the poly-Si films formed by etching in a chemical solution based on phosphoric acid. The structures of the samples were studied by Raman or microprobe Raman scattering, optical light microscopy (OM) and XRD as described in [2, 6]. The peak positions and the full-width at half-maximum (FWHM) of the Raman bands were measured with a mean error of 0.5 cm$^{-1}$. An estimate of the grain size can be deduced from both the red shift and the FWHM of the Raman peak [7]. It should be noted that accurate values for the grain size cannot be determined from the relationships described previously in the literature [7, 8], as they depend on the structures of the grains and their boundaries. Despite this, comparisons with spectra obtained from similar materials are valid. The UV hemispherical reflectance spectra in the range 250 - 400 nm were measured by a Perkin-Elmer UV/VIS/NIR Lambda 900 spectrometer.

3. Results and discussion

3.1. Influence of the annealing atmosphere

Optical micrographs of poly-Si films annealed in different ambiances using a-Si precursor are shown in figure 1. The poly-Si obtained by annealing in N$_2$ (figure 1a) have large grains (dendrites), with 20-30 µm size, separated by inter-crystalline spaces of about 10-20 µm. When annealing is performed in an atmosphere containing H$_2$ (figure 1b and c), the surface of the resulting poly-Si is very smooth. The grains are very closely packed and continuous poly-Si films are obtained. The size of the inter-grain space decreases to about 2-3 µm. The poly-Si surface in these cases is more uniform. In order to analyze the grain orientations shown in the OM-images, X-ray Diffraction Spectroscopy (XRD) measurements were performed. Figure 2 shows the XRD-pattern of a poly-silicon film. It is evident that the crystallographic peak of the silicon is (111).

![Figure 1](image_url)

Figure 1. Optical images of poly-Si films after annealing the glass/Al/a-Si structure at 500°C in: N$_2$ for 6 h (a); N$_2$+H$_2$ for 5 h (b); H$_2$ for 3 h (c). The markers correspond to 100 µm.

Microprobe Raman spectra of poly-Si layers prepared by isothermal annealing in different atmospheres at 500°C are shown in figure 3. Two spectra were measured for each sample – on the grain surface and between the grains. All of the spectra of the annealed samples have a Si-Si TO-like phonon band centered in the range 520-521.3 cm$^{-1}$, showing the presence of the Si crystalline phase only. The microprobe Raman spectrum taken from the grain (figure 3, curve 1a) of the poly-Si film prepared by annealing of the structure Al/a-Si in N$_2$ for 6 hours has a band centered at 520 cm$^{-1}$, with a FWHM of 10 cm$^{-1}$. When the annealing is performed in an atmosphere of forming gas (N$_2$+H$_2$) for 5h, the positions of both Raman peaks, from the grain surface and from the inter grain material,
Figure 2. X-ray diffraction spectrum of a glass/Al/a-Si sample annealed at 500°C in N₂+H₂ for 5 hours.

Figure 3. Microprobe Raman spectra of glass/Al/a-Si samples annealed in different atmospheres measured at intra-grain (a) and inter-grain (b) positions.

(figure 3, curves 2a and 2b) are centered at 521 cm⁻¹, with decreased FWHMs of 7 cm⁻¹ and 7.5 cm⁻¹ respectively. The narrowest Si-Si TO-like band centered at 521.3 cm⁻¹ with a FWHM of 7 cm⁻¹ (figure 3 curve 3a, 3b) is exhibited by the sample annealed in H₂ for both grain and inter-grain material. The results demonstrate that annealing in the presence of H₂ results in an improvement of the structure of both the grain and the inter-grain materials. The grain size is inversely proportional to the FWHM of the peak [9], so that one can assume that the grain size increases when the annealing has been performed in the presence of H₂, as confirmed by the OM images. The results obtained can be explained by supposing that H₂ stimulates the crystalline grain growth, probably by increasing the diffusion rates of Al and Si, which exchange their places during the AIC. It is possibly due to the reducing properties of H₂ - it reduces the Al₂O₃ film formed during the storage of the Al films in air for 24 hours before the a-Si films deposition. As a result, aluminium hydroxide is formed, leading to an enhancement of material transport. This results in an acceleration of the AIC process and an increase of the grain size in poly-Si films when annealing is performed at the same conditions, as was observed and deduced from the OM and microprobe Raman studies.

3.2. Influence of the hydrogen content in the a-Si:H precursor
To study the influence of the hydrogen content in the a-Si:H precursor, unhydrogenated (a-Si) and hydrogenated (a-Si:H) films were deposited at different substrate temperatures: RT (without heating of the substrates), 250, 300, 350 and 400 °C. Three different sets of samples were prepared with a-Si:H precursors deposited without hydrogen (a-Si) and at H₂ partial pressure of 0.05, and 0.1 Pa in the Ar+H₂ gas mixture. These conditions resulted in a hydrogen concentration in the amorphous Si precursor layers from 4 to 25 at.% (measured by ERDA [10]) and from 0 to 19 at % (calculated from IR spectra). The hydrogen concentration increased as the H₂ partial pressure was increased and the substrate deposition temperature, decreased (table 1) [11].

The Raman spectra of films obtained from a-Si or a-Si:H precursors deposited at different Tₛ, a-Si and three different hydrogen partial pressures are shown in figure 4. All of the samples display Raman spectra typical of the crystalline Si structure - a Si-Si TO band, centered between 518.5 and 520.5 cm⁻¹. The Si-Si TO peak for crystalline silicon, measured under the same conditions, is at 521 cm⁻¹ and has a FWHM of 4.5 cm⁻¹. The dependence of the Si-Si TO peak position and its FWHM (estimated from a Lorentzian fit) on the a-Si (a-Si:H) substrate temperature and the H₂ partial pressure are presented in figure 5a and figure 5b, respectively. The accuracy of the values is indicated by the error bars. As is mentioned before, the grain size is inversely proportional to the FWHM of the peak [8, 9].
Table 1. Deposition conditions of the precursor layers: φ - H concentration calculated from FTIR absorption spectra and from ERDA, respectively; θ - (111) XRD peak position; Δθ - its FWHM; D - average grain size; σ - the stress in the poly-Si films from the XRD data; ωTO - the position of the Si-Si TO-like Raman band; and its FWHM are given as well.

<table>
<thead>
<tr>
<th>Tsa-Si, °C</th>
<th>P0.12, Pa</th>
<th>φ, at. %</th>
<th>ξ, at. %</th>
<th>θ, deg.</th>
<th>Δθ, deg.</th>
<th>D, Å</th>
<th>σ, MPa</th>
<th>ωTO, cm⁻¹</th>
<th>FWHM, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>No heat.</td>
<td>0.10</td>
<td>19</td>
<td>25</td>
<td>28.44</td>
<td>0.13</td>
<td>630</td>
<td>-680</td>
<td>519</td>
<td>8.0</td>
</tr>
<tr>
<td>250</td>
<td>0.10</td>
<td>12</td>
<td>18</td>
<td>28.49</td>
<td>0.13</td>
<td>630</td>
<td>-680</td>
<td>518.5</td>
<td>7.0</td>
</tr>
<tr>
<td>300</td>
<td>0.10</td>
<td>15</td>
<td>19</td>
<td>28.49</td>
<td>0.13</td>
<td>630</td>
<td>-700</td>
<td>519.5</td>
<td>7.0</td>
</tr>
<tr>
<td>400</td>
<td>0.10</td>
<td>11</td>
<td>16</td>
<td>28.40</td>
<td>0.15</td>
<td>546</td>
<td>-393</td>
<td>520</td>
<td>7.0</td>
</tr>
<tr>
<td>250</td>
<td>0.00</td>
<td>0</td>
<td>4</td>
<td>28.50</td>
<td>0.21</td>
<td>431</td>
<td>-629</td>
<td>520</td>
<td>7.7</td>
</tr>
<tr>
<td>250</td>
<td>0.05</td>
<td>9</td>
<td>14</td>
<td>28.48</td>
<td>0.23</td>
<td>372</td>
<td>-661</td>
<td>519.5</td>
<td>7.5</td>
</tr>
<tr>
<td>300</td>
<td>0.20</td>
<td>18</td>
<td>21</td>
<td>28.50</td>
<td>0.24</td>
<td>341</td>
<td>-710</td>
<td>518</td>
<td>7.0</td>
</tr>
</tbody>
</table>

Figure 4. Raman spectra of poly-Si films obtained from a-Si and a-Si:H precursors deposited at different Tsa-Si and different H2 pressure: 0 Pa (a), 0.05 Pa (b) and 0.1 Pa (c).

Figure 5. Si-Si TO-like peak position (a) and FWHM (b) taken from Raman spectra of the samples presented in figure 4. The lines are just guides to the eye.
hand, a shift of the Si-Si TO peak position, \( \omega_{\text{TO}} \), to a lower wave number could be related to an increase in the value of the tensile stress [12]. The following tendencies can be seen. The Si-Si TO peak position shifts slightly to a higher wave number as \( T_s^{\text{a-Si}} \) is raised. This is an indication of a reduction in the tensile stress in the poly-Si samples as \( T_s^{\text{a-Si}} \) is increasing [13]. A weak tendency for increased stress in the poly-Si films, when a-Si:H precursors were used, can be noticed and could be explained by the effusion of H during the AIC. This could leave pinholes and microvoids in the poly-Si films resulting in a higher tensile stress.

The FWHM of the Si-Si TO peak passes through a minimum for poly-Si films obtained from hydrogenated precursor layers deposited at \( T_s^{\text{a-Si}} \) between 250 and 350 °C - in this case larger grains were obtained in the poly-Si films. It should be noted that we observed similar results for the AIC of glass/a-Si(a-Si:H)/Al structures [14]. During annealing, effusion of H from the a-Si:H films takes a place. It is possible to suppose that this will enhance the disorder in the a-Si:H precursor during the process of annealing. This stimulates the dissolution of Si atoms into the Al and the consecutive rearrangement into a Si crystalline structure, resulting in a higher growth rate and larger grains in the poly-Si films. This suggestion is based on the fact that the higher degree of disorder creates energetically more favourable conditions for the transformation of the a-Si:H film into a poly-Si one.

It is known that the H concentration in a-Si:H films decreases with increasing the substrate temperature, so that the precursors deposited at RT (without heating) should have a higher H content [11]. In this case, the higher quantity of effusing hydrogen probably creates conditions for an increased diffusion rate of Al and Si. Thus, intermixing of Al and Si would take place within the bulk of the resulting poly-Si film, which would inhibit the exchange between Al and Si and would lead to a lower rate of crystallite growth and a smaller grain size. Deposition of the precursor layers at temperatures > 350 °C would result in a reduced H content and in a better short range order of the a-Si:H films [12], which would slow down the re-arrangement into the crystalline structure – the poly-Si films would again have grains of a smaller size.

XRD and Raman spectra of the set of samples deposited at different \( P_{\text{H}_2} \) and \( T_s = 250 \, ^{0}\text{C} \) are presented in figures 6 and 7. One reflection peak in XRD spectra at about \( 2\theta = 28.39^0 \pm 28.48^0 \) is only observed for the poly-Si films, which corresponds to the (111) preferential orientation. The position of this peak in the c-Si is at \( 2\theta = 28.48^0 \). The intensity of the peak is higher and is at \( 2\theta = 28.48^0 \) in the poly-Si films obtained from a precursor deposited at \( P_{\text{H}_2} = 0.1 \) Pa. This observation is an indication of a better crystalline quality. The Si-Si TO-like Raman peak for c-Si is at 521 cm\(^{-1}\) with FWHM = 4.5 cm\(^{-1}\) measured under the same conditions. The shift of this peak in the poly-Si films to lower wave numbers could be due to the tensile stress in the poly-Si films, [12, 13]. The Si-Si TO-like peak position is slightly shifted to the position of the c-Si as \( P_{\text{H}_2} \) is raised to 0.1 Pa. Thus, the incorporation of H at

Figure 6. XRD spectra of poly-Si films obtained from a-Si:H precursors deposited at \( T_s = 250 \, ^{0}\text{C} \) and different \( P_{\text{H}_2} \).

Figure 7. Raman spectra of poly-Si films obtained by AIC form a-Si:H precursors deposited at \( T_s = 250 \, ^{0}\text{C} \) and different \( P_{\text{H}_2} \).
a moderate concentration in the a-Si:H precursor results in a lower tensile stress. However, a further P_{H2} increase to 0.2 Pa results in a higher stress value, probably due to the creation of pinholes as a higher amount of H effuses. The FWHM is the lowest in the films obtained from a-Si precursors deposited at P_{H2} = 0.1 Pa and 0.2 Pa (table 1). The grain size tends to increase as P_{H2} is increased to 0.2 Pa, which could be explained by the influence of the hydrogen on the layer exchange process. The higher hydrogen concentration might accelerate the diffusion of Si in the Al layer, so that grains of a larger size are obtained under identical conditions of AIC [6, 13]. It is possible to assume that the effusion of H in the precursor layer enhances the disorder in the a-Si:H precursor during the process of AIC. This stimulates the diffusion of Si atoms into the Al and the subsequent re-arrangement into a Si crystalline structure, resulting in a higher growth rate and, thus, larger grains in the poly-Si films. This suggestion is based on the fact that the higher degree of disorder is energetically more favourable for the transformation of the a-Si:H film into a poly-Si one.

Images of the surface of the poly-Si films obtained from a-Si and a-Si:H precursors deposited at different T_{a-Si}, are shown in figures 8, 9 and 10. Optical micrographs of poly-Si films prepared from a-Si precursors deposited at T_{a-Si} < 250°C show that they have smooth surfaces. Films deposited at T_{a-Si} 250, 300 and 400 °C exhibit a high density of Si precipitates (hillocks or islands) on the poly-Si surface. However, in the case of poly-Si prepared from a hydrogenated amorphous silicon precursor which the precipitates appear on the poly-Si films surface increases with the increase of P_{H2}. The presence of numerous Si islands on the poly-Si surface after AIC has been reported when the Al precursor is thicker than the amorphous silicon one, in the case of precursors of a-Si:H with high short range disorder, and of microcrystalline Si films deposited by PE CVD methods [5]. It is reasonable to suppose that the growth of the silicon hillocks in our case is a result of the better structural order in the a-Si:H precursors deposited at higher temperatures. The influence of the hydrogen concentration in a-Si:H should be taken in account as well, because it depends on the T_{a-Si} and the hydrogen pressure during the deposition. The deposition conditions of the precursor layer define the balance between the rate of the crystallite growth and the conditions for preparation of poly-Si with smooth surface.

**Figure 8.** Optical micrograph images of poly-Si films using precursor layers of a-Si:H deposited with P_{H2}=0 Pa at different T_{a-Si}: RT (a), 250 °C (b), 300 °C (c) and 400 °C (d). The markers correspond to 100 μm.

**Figure 9.** Optical micrograph images of poly-Si films using precursor layers of a-Si:H deposited with P_{H2}=0.1 Pa at different T_{a-Si}: RT (a), 300°C (b), 350°C (c) and 400°C (d). The markers correspond to 100 μm.
Figure 10. Optical micrograph images of poly-Si films using precursor layers of a-Si:H deposited with \( P_{\text{H}_2} = 0.2 \text{ Pa} \) at different \( T_s^{a-\text{Si}} \): RT (a), 300°C (b), 350°C (c) and 400°C (d). The markers correspond to 100 \( \mu \text{m} \).

The UV hemispherical reflectance spectra of the poly-Si films prepared are presented in figure 11. For comparison, the corresponding spectra of a c-Si polished wafer measured under the same conditions are also shown. The two maxima in the spectrum of single-crystalline Si at 280 nm and 365 nm are caused by optical interband transitions at the X-point (band \( E_2 \)) and along the \( \Gamma-L \) axis (band \( E_1 \)) of the Brillouin zone, respectively [15, 16]. The deviation from the UV-R spectrum of bulk crystalline Si is related to the long range order deterioration or amorphization of the material [15]. The intensity of the \( E_2 \) band (280 nm) decreases and that of the \( E_1 \) (375 nm) increases with long range disorder according to the theory of long range order relaxation effects. Additionally, at short wave-lengths, in particular at 280 nm, the reflectance is largely determined by the high value of the absorption coefficient (\( \alpha > 10^6 \text{ cm}^{-1} \)) corresponding to a penetration depth of less than 10 nm. Imperfect crystallinity in the near-surface region will cause a broadening and height reduction of this maximum [15, 16]. It is seen in figure 8a that for the poly-Si films obtained from a-Si deposited at \( T_s > 250^\circ \text{C} \) without hydrogen (\( P_{\text{H}_2} = 0 \text{ Pa} \)) the UV-R is very low in the whole photon range and smeared out maxima are observed. The maximal value of the UV-reflection and the best expressed maxima of \( E_1 \) and \( E_2 \) bands are observed for the case of using an a-Si:H precursor deposited at \( T_s^{a-\text{Si}} = 300^\circ \text{C} \) and \( P_{\text{H}_2} = 0.1 \text{ Pa} \); these values are the highest and closer to the reflection of the c-Si polished wafer – this sample has a better long range order and a better structure in the near surface region. This is in agreement with the XRD and Raman spectra and with the surface morphology observed in the optical light microscopy images.

Figure 11. UV reflectance spectra of poly-Si films obtained by AIC from a-Si:H precursors deposited at different \( T_s \) and different \( \text{H}_2 \) partial pressure: 0 (a), 0.1 (b) and 0.2 Pa (c).

3.3. Heterostructures with participation of poly-Si films
The poly-Si films were used in the Al/poly-Si/n-ZnO/n-ZnO:Al thin film heterostructure. The a-Si:H film precursor contained 9 at.% hydrogen. The isothermal annealing of the glass/Al/a-Si:H structure was performed in forming gas (\( \text{N}_2+5\%\text{H}_2 \)) at 550°C for 21 h. The ZnO (300 nm thick) and ZnO:Al
(500 nm thick) polycrystalline films were deposited by rf sputtering in Ar atmosphere [17, 18] on the surface of a p-type poly-Si layer (100 nm thick). Al and ZnO:Al were used as electrodes. The scheme of the diode heterostructure is presented in figure 12. The I-V characteristics of the heterostructure measured in dark and under illumination by a halogen lamp (20 W) are shown in figure 13. The I-V curve of the p-poly-Si/n-ZnO thin film heterostructure exhibits rectifying behavior with ratio of about 5 and photosensitivity under illumination from the side of the ZnO:Al electrode.

![Figure 12. Structural scheme of the p-poly-Si/n-ZnO:Al heterostructure.](image)

![Figure 13. Room temperature I-V curves of p-poly-Si/n-ZnO heterostructure measured in dark and under illumination.](image)

The diode turn-on voltage is about 0.2 V. The calculated ideality factor, n, was estimated to be about 2.95. The higher value of the ideality factor could be related to the presence of interface defect states between the ZnO and the poly-Si films [19, 20]. The lattice mismatch between the poly-Si and the ZnO:Al thin films leads to formation of dislocation defects at the interface. The low electrical mobility in the polycrystalline ZnO film, and the lower donor density near the surface of the ZnO grains and near the poly-Si/n-ZnO interface may be other reasons. Additionally, the partial oxidation of poly-Si during the annealing and during the deposition of ZnO result in the creation of interface states with high density whose charge states dominate the potential distribution around the interface and influence the current transport across the junction. The photosensitivity is likely to be due to the ZnO.

4. Conclusion
The results demonstrate that the structure of poly-Si films improves when AIC is performed in an atmosphere containing H\(_2\). It is assumed that H\(_2\) stimulates the crystalline grain growth during the annealing by increasing the diffusion rate of Al and Si. The study shows that poly-Si films with larger grain sizes are obtained using a precursor of a-Si:H deposited at moderate T\(_{a-Si}\) = 250-300°C and 0.05-0.2 Pa H\(_2\) pressures in the sputtering chamber. The tensile stress in poly-Si films decreases with the increase of temperature of deposition of a-Si:H precursors. The differences in the structural properties of poly-Si films could be explained by different structural order and different content of H in the precursor a-Si (a-Si:H) layers deposited under different conditions. The presented results indicate that hydrogen has an important influence on the process of AIC. The poly-Si film obtained by AIC is applied to the diode poly-Si/ZnO heterostructure with rectifying behavior.

Acknowledgements
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References