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LOW-TEMPERATURE EPITAXIAL Si ABSORBER LAYERS GROWN BY ELECTRON-CYCLOTRON RESONANCE CHEMICAL VAPOR DEPOSITION

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ABSTRACT

We studied the homo-epitaxial growth of Si layers on crystalline Si(100) substrates in the temperature range from 420 °C to 510 °C using electron-cyclotron resonance chemical vapor deposition (ECRCVD). Above 480 °C the films grew epitaxially. Films deposited with a growth rate of 15 nm/min at 510 °C are of excellent crystallographic quality up to layer thicknesses as large as 2.23 μm. With increasing thickness local highly defective regions were formed in the epitaxial films. They are cone-shaped and consist of thin polycrystalline needles only. An abrupt breakdown of epitaxial growth as usually reported in literature was not observed. The non-intentionally doped films are n-type independently on the substrate temperature. The film/substrate interfaces were analyzed by I-V measurements.

1 INTRODUCTION

An attractive low-temperature route to a polycrystalline Si thin-film solar cell on glass bases on a seed layer concept. In such a cell concept, we use a thin large-grained polycrystalline Si seed layer on glass formed by aluminum-induced crystallization (AIC) [1]. The absorber layer is grown on this seed layer in a subsequent epitaxial growth process. The substrate temperature of such a growth process is limited by the glass to temperatures of about 600 °C.

At such low temperatures it becomes necessary to use deposition techniques which provide additional energy to the surface of the growing film. Ion-assisted techniques like electron-cyclotron resonance chemical vapor deposition (ECRCVD) [2] or ion-assisted deposition (IAD) [3] have shown previously that such methods are apt for low-temperature epitaxial growth of Si. Already first success was reported of growing Si epitaxially on AIC seed layers using IAD [4]. While IAD is an ultra high vacuum (UHV) process ECRCVD works at an usual base pressure of 10^{-7} Torr.

Low temperature Si epitaxy is in general accompanied with an increasing surface roughening, the formation of amorphous inclusions and finally a complete breakdown of epitaxy at a specific critical thickness [5, 6]. This process is known to be a function of the deposition process, the substrate orientation and temperature. For ECRCVD critical thicknesses are reported to be in the range of several hundreds of nm for Si(100) substrates [7] and essential smaller for other substrate orientations [8]. A less abrupt worsening of a 1.3 μm epitaxial Si film on Si(100) was observed by Platen *et.al* [8] but also accompanied by the formation of amorphous regions. Following a solar cell concept based on an epitaxial thickening of a seed layer to form the absorber layer at low temperatures, it is necessary to grow Si films of good crystal quality with higher thicknesses as the above mentioned.

In order to understand and optimize the growth conditions for crystalline Si absorber layers with a thickness of a few μm at such low temperatures, we investigated the homo-epitaxial growth of Si on Si wafers using ECRCVD. Here we report on Si growth in the temperature range 420 - 510 °C concentrating onto the growth on Si(100) wafers.

2 EXPERIMENTAL

The films were grown in an ECRCVD system with a RR 250 PQ (Roth & Rau, Germany) plasma source. We used CZ-Si(100) wafers (p-type, 5 Ωcm) as standard substrates. First, the substrates were cleaned by a standard RCA pro-

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cedure. A final HF dip (30 s, 2 % HF solution) was carried out to remove the native oxide and passivate the substrate surface directly before the specimens were transferred into the process chamber via a load lock. Prior the deposition, the substrates were hold in hydrogen atmosphere (3.2 mTorr) for 20 min to obtain stable thermal process conditions. All films were grown only changing the substrate temperature. The other process parameters, like microwave power (1000 W), total pressure (6.5 mTorr) and gas fluxes were kept constant. A remote plasma gas (50 sccm H_2) was used. The process gas consisted of 10 sccm SiH_4 and 10 sccm H_2. The substrates were always grounded. The base pressure of the system is about 4×10^{-7} Torr at process conditions. The growth rates were determined by a step profiler.

Rutherford Backscattering (RBS) measurements were carried out in order to analyze the structural properties of the grown films. The RBS channeling spectra were recorded at the Tandetron accelerator JULIA of the University of Jena (Germany). The $\langle 100 \rangle$ axis of the Si substrate was aligned parallel to the direction of the incident ion beam (1.4 MeV He^+). The disorder depth profiles were calculated from the aligned spectra using a linear approximation for the dechanneled ions as described in [2].

The film morphologies were analyzed by scanning (SEM) and transmission electron microscopy (TEM), respectively. For SEM an Hitachi S4100 (25 kV) was used. The TEM measurements were carried out with a TENCAI F20 mono of the TU Delft (The Netherlands).

For electrical investigations I-V and Hall measurements were carried out. For I-V measurements mesa structures (1 to 1.8 mm in diameter) with magnesium front contacts were prepared to define the junction area. An aluminum layer served as back contact. To determine the carrier density, Hall measurements were performed on films grown on highly ohmic substrates (p-type, 3 kΩcm) using magnesium contacts.

3 RESULTS AND DISCUSSION

3.1 Structural Properties

To investigate the influence of the substrate temperature on the structural qualitiy we deposited Si films in the temperature range from 420 °C to 510 °C. We observed a strong dependence of the structual quality on the temperature. Figure 1 shows the RBS disorder depth profiles of 800 nm thick films grown at different substrate temperatures. At temperatures above 480 °C the films are always of excellent crystallographic quality within the measurement accuracy of RBS (disorder ≈ 0). A worsening of the crystallographic quality with temperatures below 480 °C was observed due to an increase of disorder in the films (disorder > 0). The disorder of the films increases significantly with increasing layer thickness already starting at the interface.

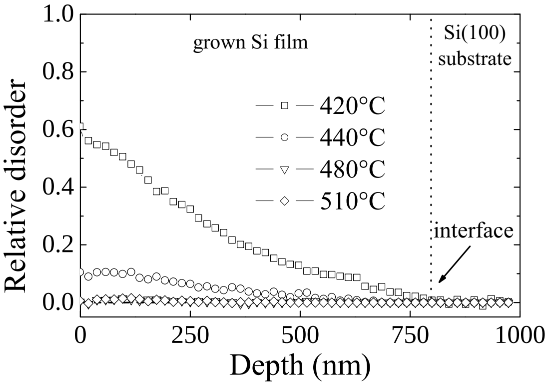

Fig. 1 Disorder depth profiles of 800 nm thick Si films grown on Si(100) wafers at different substrate temperatures. At 480 °C and 510 °C the films are of perfect crystallography. Below 480 °C the crystallographic disorder increases significantly starting already at the interface.

It is known, that the quality of an epitaxially grown Si film strongly depends on the film thickness. Therefore we investigated the epitaxial growth as a function of layer thickness. We prepared Si films of different thicknesses with a growth rate of 15 nm/min at 510 °C. An excellent crystallographic quality was observed at this temperature at a 800 nm film as seen in Fig. 1. From RBS measurements we determined the minimum yield (χ_{min}) as a figure of merit for the structual perfection of these films close to the surface. The RBS χ_{min} is plotted as a function of layer thickness in Fig. 2. The quality of the epitaxial growth decreases only very slightly for thicker

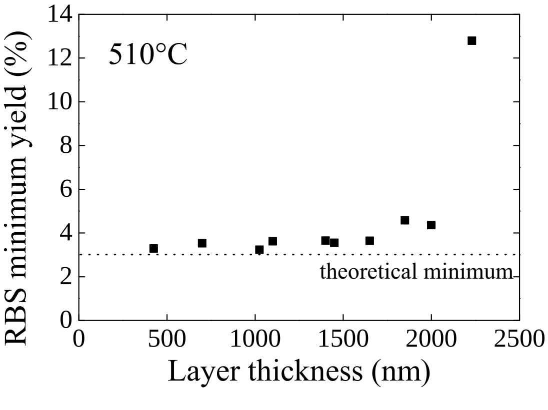

Fig. 2 RBS minimum yield as a function of layer thickness of films grown on Si(100) at 510 °C. The disorder increases only very slightly with film thickness up to thicknesses of 2 μm.

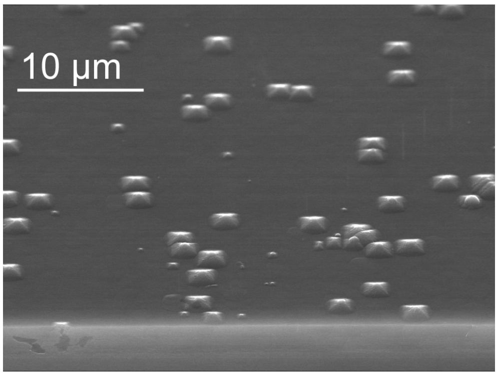

Fig. 3 SEM image of a 2.23 μm thick Si layer grown on Si(100) at a temperature of 510 °C. The image shows the cross section and the surface under 30 ° tilt. Local defect structures in the grown film are observable.

films up to a thickness of 2 μm. The observed χ_{min} are close to the theoretical minimum determinded by measurement system. Although above this thickness the minimum yield increases more rapidly from about 3 - 4 % to 12.7 % the increased χ_{min} still indicates a good structural order of the total film.

Analyzing the grown films by SEM, we observed hillocks on the film surface starting at thicknesses of approximately 1 μm. Figure 3 shows a SEM image of the 2.23 μm thick absorber layer grown on Si(100) with such locally existing hillocks. The image shows the cross section and the surface under 30 ° tilt. Apart from the hillocks, surface and cross section are smooth pointing to the good structural quality of the rest of the film. By TEM measurements we determined these hillocks as the top of a local highly defective region. A TEM cross section of such a region is shown in Fig. 4. The defective region is cone-shaped and seems to start at or very close to the film/substrate interface. From the TEM image it is not possible to determine the exact starting point of such a cone because there is no information whether the performed cut for TEM preparation matches the minimum of a cone exactly. The defective region consists of polycrystalline silicon which is formed by thin needle-like crystals, grown always perpendicular to the interface. These needles are approximately 20 nm in diameter and 160 nm long as not shown here in detail. No amorphous phase was observed. The edges of the defective region are surrounded by nanotwins with a thickness of 3-5 monolayers. The nanotwins, which are shown in the inset of Fig. 4, reduce the stress between the epitaxial film and the polycrystalline cone. Changes in bond length due to stress at this site were prooved by means of electron energy loss spectrometry and are published elsewhere [9]. Outside the defect region stacking faults are seen in the film. Raman measurements give also no evidence of an amorphous phase within these films.

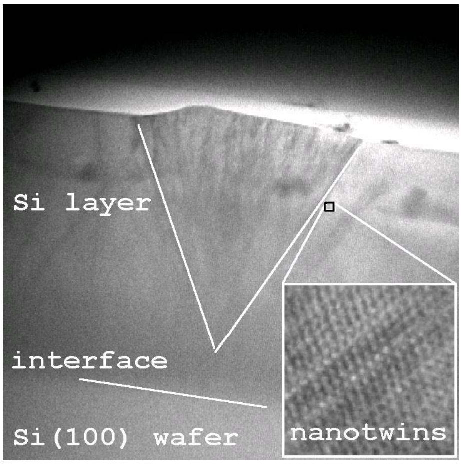

Fig. 4 TEM cross section of a local defective region of the 2.23 μm film starting right at the interface epitaxial film/substrate. The inverse cone is polycrystalline and consists of crystal needles perpendicular to the interface. No amorphous phase was observed. The cone is surrounded by nanotwins (inset).

Our investigations show, that there is no typical breakdown of epitaxy (i.e. abrupt transition from epitaxial to amorphous growth) after a critical thickness in our films up to 2.23 μm. From the only slow worsening of structural quality the successful epitaxial growth of thicker films as reported here are expected for the future.

3.2 Electrical Properties

To prepare absorber layers of a Si thin-film solar cell it is necessary to analyze not only the structural quality of the grown films but also the electrical properties. Therefore the type of conductivity and the carrier density of the films were determined by Hall measurements. The non-intentionally doped films turned out to be n-type. The electron density is in the range of some 10^{16} cm^{-3} only slightly varying with the substrate temperature. The origin of this n-type conductivity is still under investigation. One reason could be the formation of thermal donors.

To analyze the film/substrate interfaces in more detail we used pn-junctions performed by the p-type Si(100) substrates and the n-type films. Investigating the I-V characteristics of such junctions we observed a strong dependence of the interface on the substrate temperature. In Fig. 5 the I-V curves of two samples are exemplarily shown prepared at 420 °C and 480 °C. The I-V curves of the samples prepared at temperatures below 480 °C exhibit an ohmic behavior which can be explained by the existence of shunts at

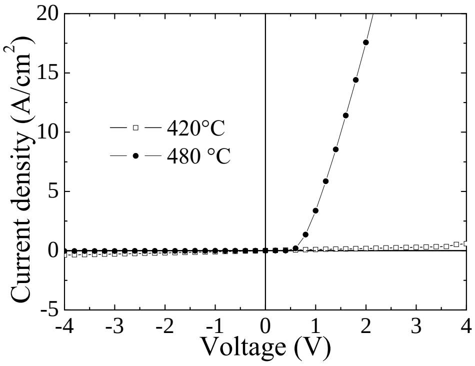

Fig. 5 I-V characteristics of grown Si film/p-type Si(100) substrate junctions prepared at 420 °C and 480 °C, respectively. The film grown at 480 °C shows the typical characteristic of a pn-diode whereas the film grown at 420 °C has an ohmic behavior.

the interface. Almost all of the samples prepared at temperatures above 480 °C show, however, the typical characteristic of a pn-diode. Due to an improved interface between the substrate and the deposited absorber layer the shunts are strongly reduced. This is in accordance with the improved crystallograhic quality of the films at temperatures at 480 °C and above.

4 SUMMARY AND CONCLUSIONS

In conclusion, we studied the low temperature Si growth by ECRCVD for epitaxial Si absorber layers on Si(100) wafers at various temperatures by investigating morphological and electrical properties, respectively. We are able to grow epitaxial Si films on Si(100) with thicknesses of 2.23 μm at 510 °C. As far as we know, this is the largest film thickness grown epitaxially by ECRCVD at such low temperatures. In contrast to most of the reported investigations, we did not observe an abrupt and complete breakdown of epitaxy combined with turning the growth mode from epitaxial into amorphous growth. We found only a slightly worsening of the structural quality by the formation of local defective cones of polycrystalline nature. This prooves, that ECRCVD is a suitable technique to grow epitaxial Si(100) films thick enough to act as absorber layers in a Si thin film solar cell concept.

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