LOW-TEMPERATURE EPITAXY FOR THIN-FILM SILICON SOLAR CELLS BY ECRCVD – STRUCTURAL AND ELECTRONIC PROPERTIES

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ABSTRACT

The homo-epitaxial growth of crystalline Si films at low temperatures by electron-cyclotron resonance chemical-vapor deposition is studied. The presence of boron in the process is found to impede the crystal growth and facilitates the formation of extended defects, which can be made visible by defect etching. The analysis of the resulting etch pits by scanning electron microscopy reveals a high density of structural defects like dislocations and stacking faults. A correlation between the density of a pyramid-shaped etch pit and the photoluminescence spectra is discussed. The density of this etch pit was found to depend on substrate temperature and boron concentration. First solar cell results with an epitaxial grown boron-doped absorber layer are presented.

INTRODUCTION

Solar cells made of thinned-down silicon wafers have shown the high potential of thin-film silicon for high efficiency cells [1]. But it is to be expected that only real thin-film technologies with absorber thicknesses of a few micrometer on large-area low-cost substrates (such as glass) will lead to a significant cost reduction of photovoltaic modules. One promising approach is the realization of a polycrystalline Si (poly-Si) solar cell based on an epitaxially thickened seed layer on glass [2]. The use of glass substrates limits the process temperatures of all process steps to values below the softening point of the glass which is close to 650 °C. At these low temperatures it becomes necessary to apply deposition techniques which provide additional non-thermal energy to the surface of the growing film. It has been demonstrated that ion-assisted techniques like electron-cyclotron resonance chemical-vapor deposition (ECRCVD) [3] or ion-assisted deposition [4] are in principle suitable for low-temperature Si epitaxy but several difficulties have to be overcome. For instance, crystal orientation and surface cleaning of the substrates are much more critical for low-temperature epitaxial growth than for conventional thermal chemical-vapor deposition at high temperatures.

As shown recently, non-intentionally doped Si films can be grown epitaxially by ECRCVD on Si(100) substrates up to thicknesses of 2.5 µm with high structural quality [5]. In this work, we compare the low temperature epitaxy of boron-doped with non-intentionally doped Si on Si(100) wafers by ECRCVD. The structural and electronic properties of the grown films were characterized by a variety of techniques.

EXPERIMENTAL

The films were grown in an ECRCVD system with a RR 250 PQ (Roth & Rau, Germany) plasma source. As substrates Si(100) wafers were used with different resistivity and type of conduction. At first, the substrates were cleaned by a standard RCA procedure. A final HF dip (30 s, 2% HF:H_2O 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 to deposition, the substrates were held in a hydrogen atmosphere (3.5 mTorr) for 20 min to obtain stable thermal process conditions. For all experiments a microwave power of 1000 W and a total pressure of 7 mTorr were used. H_2 was used as excitation gas. The process gas consisted of silane, hydrogen and diborane diluted in H_2 (0.5 %). The substrate temperature was varied in the range from 510 °C to 580 °C. The resulting growth rate was about 18 nm/min. The base pressure of the system was about 4×10^{-7} Torr at the process temperature.

To investigate the structural properties of the grown films, a Hitachi S4100 (25 keV) scanning electron microscope (SEM) equipped with a cold field emission cathode was used. For a detailed investigation of the sample cross section transmission electron microscopy (TEM) experiments were carried out (TENCAI F20 mono). Secondary ion mass spectrometry (SIMS) profiles were measured to determine the boron as well as certain impurity concentrations in the deposited films. For electrical investigations capacitance-voltage (CV) and Hall effect (HE) measurements were carried out. CV measurements were performed on films either grown on phosphorus-doped (70-130 mΩcm) CZ-Si wafers with Au Schottky contacts (non-intentionally doped films) or on boron-doped (2-5 mΩcm) CZ-Si wafers with Al Schottky contacts (boron-doped films). In both cases Au back contacts were used. For HE measurements we investigated films grown on weakly boron-doped (3 kΩcm) FZ-Si substrates with magnesium contacts. Defect etching experiments and photoluminescence (PL) measurements at 5 K were carried out. The PL spectra were obtained using an Oxford Optistat flow cryostat. The samples were excited by the 514 nm line of an argon-ion laser (10

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W/cm²). The PL emission was analyzed by a single grating monochromator (Amko-LTI 01-002, resolution: 3 nm) and detected by an InGaAs detector. Defect etching was performed using Secco etch (50 % HF : 0.15mol/l $K_2Cr_2O_7$, ratio 2:1). The samples were etched for 10 s and the resulting etch pits were analyzed by SEM.

RESULTS AND DISCUSSION

Epitaxial growth of non-intentionally doped Si

As reported recently [6], non-intentionally doped, epitaxially grown Si films will have local defective structures if they are grown by ECRCVD at low temperatures. These defective regions (see example shown in Fig. 1) have the shape of an inverse pyramid and start to grow at or very close to the film/substrate interface. They also have a pyramid-like extension at the sample surface with a squared basis (inset of Fig. 2). They consist of small-grained polycrystalline silicon which is formed by thin needle-like crystals (20 nm diameter, 120 nm long), grown perpendicular to the interface. No amorphous phase was observed as in earlier repots [3]. In the surrounding crystalline region a high density of nano twins was observed by atomic resolution TEM. The density of these pyramid-shaped regions decreases with increasing substrate temperature but even at 580 °C they could not be avoided completely so far.

Extended defects like the pyramid-shaped defective regions, dislocations or stacking faults can be made visible by etching the surfaces of the samples by concentrated Secco etch. Secco etch preferentially etches the distorted regions around extended defects. This results in etch pits which can be further analyzed by SEM. An overview is given in Fig. 2 for a 1 µm thick Si film grown at 560 °C. For comparison an as-grown Si film is shown in the inset (same magnification) containing a pyramid-like defect. In the right part of the main image a large etch pit (D_P) can be seen, which results from etching of such a defective growth region. Although the surrounding surface around the pyramid is smooth in the as grown state several additional etch structures of different shapes and sizes (from 100 nm to a few µm) became visible after Secco etching. The total etch pit density for samples grown at 560 °C is in the order of 10^8 cm^{-2} whereas the density of the pyramid-like defects is in the range of 10^5 cm^{-2}.

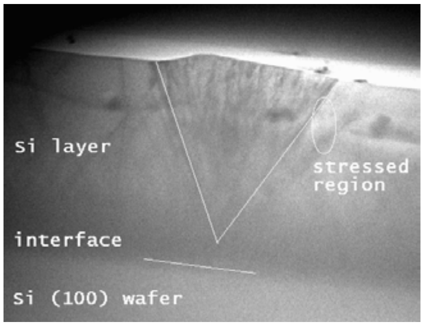

Fig. 1: TEM cross section of a local defective region (T_S = 510 °C, thickness: 2.2 µm). Due to TEM specimen preparation the pyramid-like extension was polished off.

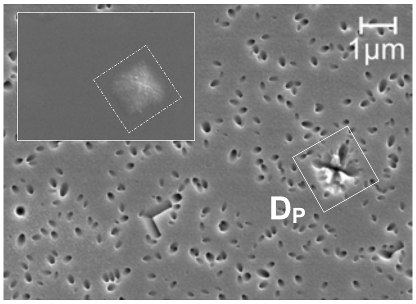

Fig. 2: SEM image of a Secco-etched surface of an epitaxially grown Si film without intentional doping (T_S = 560 °C). Inset: the film surface prior to the etching containing a pyramid-like defect (same magnification).

In order to obtain more information about the defects in the films, PL measurements were carried out prior to defect etching. A typical PL spectrum (at T = 5 K) is shown in Fig. 3 for a 1 µm thick Si film grown at 560 °C. Three PL-peaks (P1: 0.885, P2: 0.903 and P3: 1.114 eV) were identified as contributions from the epitaxial layer [7]. The relative intensities of these peaks vary strongly for different samples, which supports the view that they stem from different defects or impurities. A reason for this variation may be in part a non-optimized reproducibility of the growth process. The emissions at 1.040 and 1.090 eV are phonon-replica of boron-doped excitons in the Si substrate.

A detailed analysis of different kinds of etch pits and the correlation to the PL spectrum can be found elsewhere [7]. Most of the etch pits are probably due to dislocations or stacking faults. Although the PL intensities of P1 and P2 and the densities of two kinds of elliptical etch pits appears to be linked, it is not clear whether these emissions are caused by recombination at these defects.

The thin layers were also investigated by HE measurements. We observed n-type conductivity with typical values of the free electron concentration n in the range of $(5–30) \times 10^{15}$ cm^{-3} at room temperature (RT). From CV measurements we obtained similar values and homogenous doping depth profiles. So far the origin of this base doping could not be identified. However, SIMS

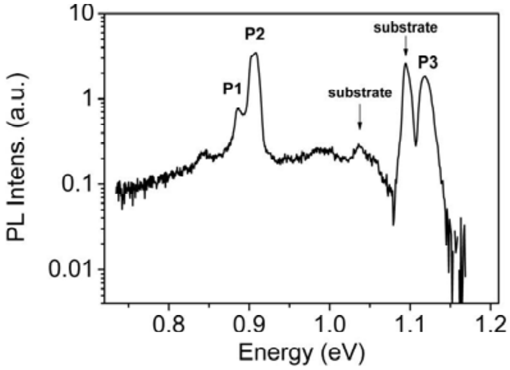

Fig. 3: PL spectrum (T=5 K) of an non-intentionally doped, epitaxially grown Si film on a Si wafer (T_S = 560 °C). The three luminescence peaks P1, P2 and P3 are contributions from the deposited layer.

measurements showed, that samples with higher concentrations of impurities such as oxygen and nitrogen also have higher electron concentrations. We therefore attribute this doping to a contamination with these impurities.

The RT electron mobility μ_n varied between 400 and 800 cm^2/Vs in our samples. On average, these μ_n values are about 50 % lower than in an ideal n-Si crystal of comparable doping level without extended defects. A similar difference between the experimental μ_n data and theoretical values based only on phonon and impurity-related scattering mechanisms was found in temperature-dependent HE measurements.

Epitaxial growth of boron-doped Si

For the epitaxy of p-type Si films diborane diluted in hydrogen was added to the process gas. The layers grown at the same temperature (T_S = 560 °C) but with 100 ppm $[B_2H_6]/[SiH_4]$ showed much more disordered growth regions and other crystal defects than the comparable non-intentionally doped films. The resulting SEM image of this sample after Secco etching (Fig. 4*A*) differs significantly from the one in Fig. 2. The Secco etch reveals a very high density of large etch pits similar to the etch pit D_P in Fig. 2 (> 10^8 cm^{-2}). This obviously indicates that the majority of the Si film consists of the corresponding pyramid-shaped defects.

It is well known, that the introduction of boron into a low-temperature Si CVD process strongly impedes the epitaxial growth [8]. Nevertheless, the formation of boron-oxygen complexes usually seen as responsible for such a effect should be unstable above 500 °C.

In order to improve the quality of the Si film, both substrate temperature and diborane concentration were varied. By increasing the substrate temperature from 560 °C to 580 °C the conditions for epitaxial growth improve significantly. Only very few etch pits of type D_P could be observed. Their density is reduced to the same value as obtained by non-intentionally doped films (10^5 cm^{-2}). As shown in Fig. 4*B*, the etched surface of the boron-doped sample with 100 ppm $[B_2H_6]/[SiH_4]$ grown at 580 °C looks very similar to that of the non-intentionally doped film (Fig. 2). Lines, vertical holes and a large number of additional smaller etch pits can be identified again. Only the density of the small pits is increased by approximately a factor of 2. If the boron concentration is increased to 200 ppm $[B_2H_6]/[SiH_4]$ the quality of the grown film decreases again (Fig. 4*C*). The density of the D_P type etch pits is raised significantly (10^7 cm^{-2}).

The PL spectra of the samples *A*, *B*, and *C* proir to Secco etching are shown in Fig. 5 obtained under the same experimental conditions. All spectra are dominated by the substrate luminescence at 1.09 eV. Although we found also etch pits similar to the ones related to P2 in the non-intentionally doped films (not visible with magnification of Fig. 4), we did not observe any of the three separate emission lines P1 to P3. Instead, a broad emission band below 0.90 eV and two emission bands around 1.0 eV were detected. The intensity of these emission is correlated with the structural quality of the Si layer. Sample *A* with the highest density of pyramid-shaped defects shows the highest luminescence intensity at low energies, whereas the emission intensity of the film grown at 580 °C with 100 ppm $[B_2H_6]/[SiH_4]$ in this spectral region is rather low (sample *B*). The results indicate that the PL emission around 0.8 eV could originate from the small-grained crystalline phase of the pyramid-shaped defects. This is in agreement with Ref. [9] where a broad emission at 0.8 eV is attributed to a microcrystalline Si phase with a grain size of about 20 nm.

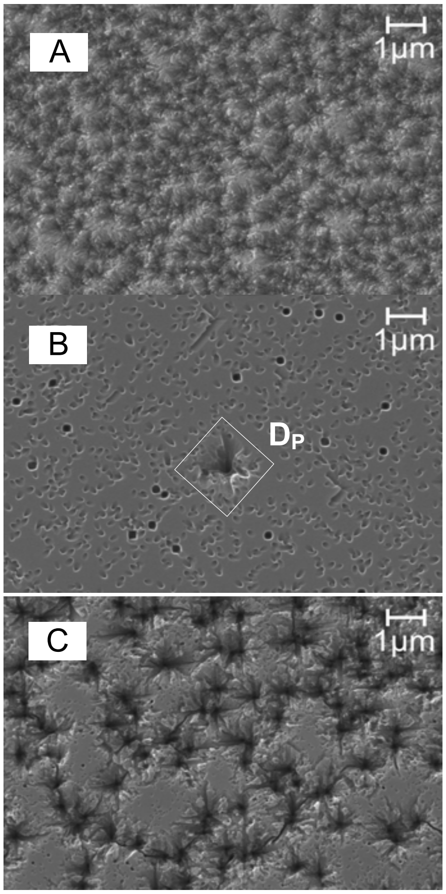

Fig. 4: SEM images the Secco-etched surfaces of Samples *A* (560 °C, 100 ppm $[B_2H_6]/[SiH_4]$), *B* (580 °C, 100 ppm $[B_2H_6]/[SiH_4]$), and *C* (580 °C, 200 ppm $[B_2H_6]/[SiH_4]$).

The origin of the two-band PL emission of samples *B* and *C* around 1.0 eV is not identified so far. Due to the fact, that the sample with the lowest amount of small-grained crystalline regions (*B*) showed the highest PL intensity in this spectral region and that sample *A* has no emission at these energies it is concluded that this luminescence may originate from recombination centers outside of the pyramid-shaped defective regions.

The difference in intensity of the substrate-related emission at 1.09 eV between sample *B* with a high intensity and samples *A* and *C* with a much lower PL signal could not be explained so far. One reason could be a higher interface recombination of the samples *A* and *C* where the epitaxial growth starts already strongly disturbed.

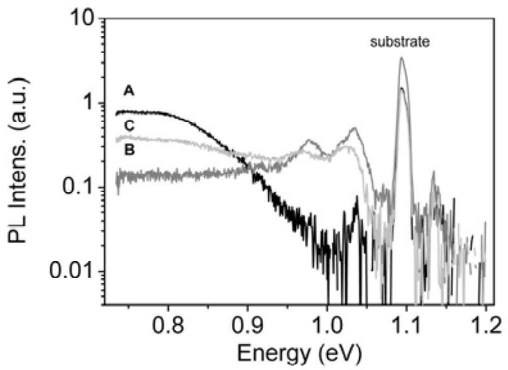

Fig. 5: PL spectra (T=5 K) of boron-doped epitaxial grown Si films *A* (560 °C, 100 ppm $[B_2H_6]/[SiH_4]$), *B* (580 °C, 100 ppm $[B_2H_6]/[SiH_4]$) and *C* (580 °C, 200 ppm $[B_2H_6]/[SiH_4]$).

SIMS analyses were carried out to investigate the boron incorporation. It is found that the incorporation efficiency from the gas phase composition into the film amounts to about 15 % (3×10^{18} cm^{-3}) for 100 ppm $[B_2H_6]/[SiH_4]$. In order to determine the part of boron atoms which is electrically active in the film CV measurements were carried out. We obtained p-type conductivity and a homogeneous acceptor concentration of about 3×10^{15} cm^{-3}. These results show, that the doping efficiency is of about 0.1 %. This may be explained by a non-substitutional incorporation of boron into the Si lattice.

Solar cell results

First solar cell structures were prepared using p^+-type Si(100) wafers (5mΩcm) as substrates. After the epitaxial growth of 2 µm boron-doped Si (prepared as sample *B*, $N_A = 3 \times 10^{15}$ cm^{-3}) 20 nm of hydrogenated amorphous Si (phosphorus-doped, 2500 ppm gas phase concentration) and as a window layer about 80 nm ZnO were deposited. Aluminum was used for the front and back contacts in a mesa-etched structure. Open circuit voltages of about 330 mV were obtained. These values were reached without additional hydrogen passivation of the epitaxial absorber or further thermal treatments. It is clear that due to the high defect density of the absorber layer the efficiencies are still rather low.

SUMMARY AND CONCLUSIONS

We have studied the quality of both non-intentionally and boron-doped Si films grown epitaxially at low temperatures by ECRCVD. The presence of boron in the process impedes the crystal growth and facilitates the formation of extended defects within the temperature range from 510 °C to 580 °C. PL measurements, Secco etching and SEM analyses were carried out to characterize the deposited films. Although clearly defect related PL emission bands have been found there is so far no link to specific recombination centers. A reduction of a specific pyramid-shaped defect could be obtained at higher substrate temperatures and lower boron concentrations. First solar cell structures with an boron-doped absorber were prepared. Considerably improvement of the structural quality of the epitaxial growth will be required in order to realize efficient thin-film silicon solar cells with a low-temperature epitaxial absorber grown by ECRCVD.

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