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ELECTRONIC PROPERTIES OF LOW-TEMPERATURE EPITAXIAL SI GROWN BY ECR-CVD

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ABSTRACT: Low-temperature epitaxial thin silicon films were deposited in the temperature range between 420 and 600 °C by electron cyclotron resonance chemical vapor deposition (ECR-CVD). Electron concentrations between 10^{15} and 10^{17} cm^{-3} and carrier mobilities of up to 850 cm²/Vs were determined by Hall effect measurements. The electron concentration at ambient temperature was found to correlate with the spin density of an electron spin resonance signal at $g = 1.999$ that is detected at 5 K. Deep level transient spectroscopy showed the presence of at least 6 deep levels in the upper part of the forbidden gap. Extended defects were analyzed by scanning electron microscopy on Secco-etched films. Photoluminescence spectra taken at low temperatures show several bands one of which seems to be related to an extended defect.

Keywords: Si-Films, Characterisation, Defects

1 INTRODUCTION

In the long term, crystalline thin-film silicon solar cells are promising for a cost-effective implementation of photovoltaic concepts for environmentally friendly energy generation. The approaches pursued in our group involve the epitaxial thickening of c-Si seed layers produced e.g. by aluminum-induced crystallization or laser crystallization on glass substrates. In order to gain information on the electronic properties of low-temperature epitaxial thin silicon films without having to process complete solar cells, we investigated such films grown on (100) Si wafers. Films were deposited in the temperature range between 420 and 600 °C by electron cyclotron resonance chemical vapor deposition (ECR-CVD). As reported earlier [1], good crystallographic quality was obtained in films grown at temperatures at 480 °C and above.

Carrier mobility is a basic property of the absorber layer used in devices such as thin-film solar cells. The mobility is decreased by the presence of defects in the host materials. On the other hand, shallow and deep levels of point defects and extended defects such as dislocations are able to deteriorate the minority carrier lifetime in such a way that the solar cell efficiency is reduced.

In this paper, we report and discuss the results of defect analysis of these non-intentionally doped layers, which showed n-type conductivity. They were obtained using a variety of methods: Hall effect (HE) measurements, capacitance voltage (CV) profiling, deep level transient Fourier spectroscopy (DLTFS), electron spin resonance (ESR) measurements, and photoluminescence (PL) measurements. Additional information on extended defects was obtained by Scanning Electron Microscopy (SEM) on Secco-etched samples.

2 EXPERIMENTAL

ECR-CVD is an ion-assisted CVD process enabling epitaxial growth of Si layers with a thickness of up to 2.5 µm on (100) Si wafers at temperatures below 600 °C [2]. A typical thickness of samples investigated here is 1 µm. Details of the ECR-CVD deposition process were described earlier [1].

HE measurements were performed in a standard van der Pauw configuration. To avoid substrate influence layers on high-resistivity p-type Si substrates were investigated. The quality of the separating pn junction was checked by vertical current-voltage measurements on mesa-etched structures made from the same layers investigated in HE measurements.

For capacitance-based methods, Au Schottky diodes were prepared on HF dipped layers grown on low-resistivity n-type Si substrates with Mg back contacts. A Biorad DL-8000 system was used for CV and DLTFS measurements. ESR measurements were carried out using a continous-wave X Band (9.5 GHz) Bruker Elexsys 580 spectrometer and the samples were cooled in a He-flow cryostat. Determination of the spin density was achieved by comparison to a reference sample (P-doped c-Si) with known P concentration. PL was excited by the 514 nm line of an argon ion laser in a He-flow cryostat and recorded by an InGaAs detector. The resolution of the PL set-up was limited by the resolution of the monochromator and is estimated to be about 5 nm. The ESR and PL data presented here were all recorded at 5 K.

3 RESULTS

3.1 Carrier concentration and CV profile

HE measurements show that the nominally undoped layers have typical electron concentration in the range $5 - 20 \cdot 10^{15}$ cm^{-3} at room temperature (RT) if they were grown under optimized growth chamber conditions. Similar values are obtained from CV profiles $N_d(x)$, which are homogenous. However, in layers grown directly after cleaning the growth chamber $n > 10^{17}$ cm^{-3} is observed and $N_d(x)$ shows strong variations within the layers. On the other hand, the growth temperature was not found to play an important role in the temperature range used.

Hall mobility values μ_H at RT are shown in Fig. 1. A typical value is 600 cm^2/Vs. Variations between 400 and 850 cm^2/Vs are observed. Whereas the mobility in layers with high carrier concentration ($n > 10^{17}$ cm^{-3}) reaches 80 – 90 % of the theoretical maximum μ_H does not increase significantly as would be theoretically expected in layers with $n \leq 10^{16}$ cm^{-3}. Additionally, mobility curves $\mu_H(T)$ obtained from temperature dependent HE measurements

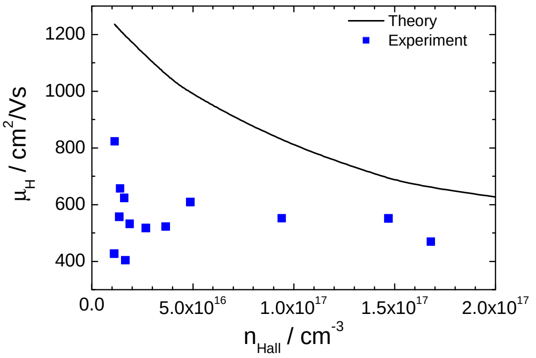

Figure 1: Hall mobility at room temperature versus carrier concentration. The line represents the Hall mobility in ideal c-Si wafers.

down to 30 K cannot be fitted correctly under the assumption that the mobility is only determined by phonons and scattering by neutral and ionized impurities. Both observations indicate the presence of extended defects (see also 3.5).

3.2 ESR

A typical ESR spectrum recorded at 5 K is shown in Fig. 2. Generally two resonances are visible that have their origin in the epitaxially grown layers: One at a g-value of g = 2.005-2.006 (called “db”) which probably stems from dangling bond-like defects and a second one at g = 1.998-1.999 (called “dd”) which stems from a localized state near the conduction band, probably a donor state. Both ESR lines are within the accuracy of the X band measurement isotropic, have a lorentzian line shape, and hardly saturate in the investigated microwave-power range up to 200 mW.

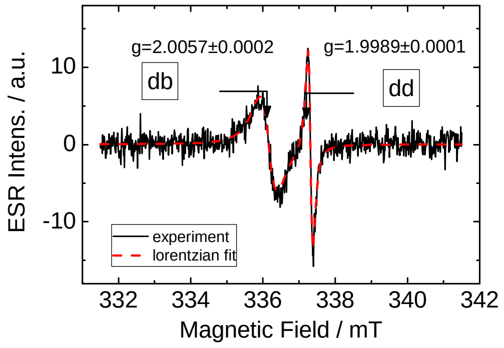

Figure 2: ESR spectrum recorded at 5 K showing two resonances: the db resonance at g = 2.005 - 2.006 and the dd resonance at g = 1.998 - 1.999.

The spin density N_{dd} of these dd centers was determined and is found to correlate with the carrier concentrations n_{Hall} measured at 300 K. We observe a one to one correlation over two orders of magnitude in carrier concentration as shown in Fig. 3. This behavior can be understood in a very simple model.

At room temperature all shallow donors and acceptors are ionized. From HE measurements we therefore obtain $n_{Hall} = N_D - N_A$ with N_D and N_A being the donor and acceptor concentration, respectively. When the sample is cooled to 5 K, we assume that as many donors become occupied, as free charge was present at room temperature. Only some donors will remain ionized due to the acceptors present in the material. Since the occupied (neutral) donors are paramagnetic, they will produce the observed dd ESR resonance. Therefore, we observe the identity $N_{dd}(5K) = N_D - N_A = n_{Hall}(300K)$.

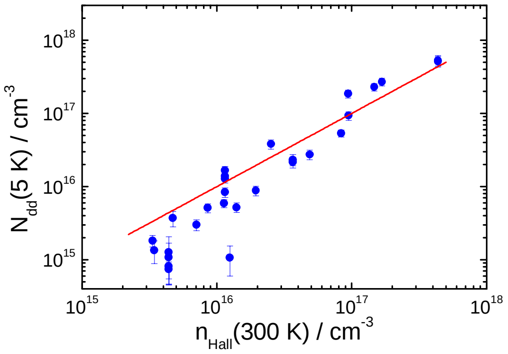

Figure 3: Comparison of the measured density of dd-centers at 5 K and the charge carrier concentration at room temperature. The line is the identity function $N_{dd} = n_{Hall}$.

3.3 DLTFS

A DLTFS spectrum measured with -5 V bias, 100 ms pulse duration, and 100 ms transient recording time is shown in Fig. 4. Several deep levels named L1 to L6 here are detected in the upper part of the forbidden gap. L2 is the dominant line present in all samples investigated with concentrations in the 10^{14} - 10^{15} cm^{-3} range. Annealing experiments up to 900 °C showed no significant reduction of the L1 concentration. The activation energies of L1, L2, and L3 were determined from Arrhenius plots of the electron emission data with 0.18 eV, 0.27 eV, and 0.54 eV, respectively. Electron capture cross sections in the range 10^{-15} to 10^{-16} cm^2 were derived from the same data. Further emission lines coming from traps with lower concentrations could not be resolved clearly due to superposition effects.

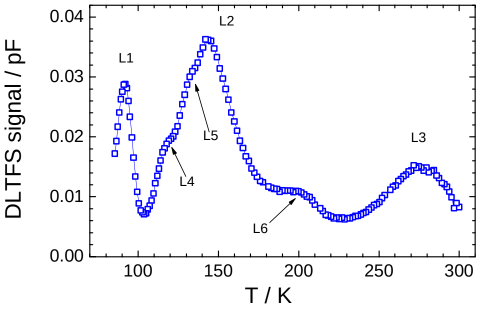

Figure 4: DLTFS spectrum of an epitaxial Si layer measured with -5 V bias, 100 ms pulse duration, and 100 ms transient recording time.

3.4 PL

A typical PL spectrum recorded at 5 K is shown in Fig. 5. Three lines at 0.88, 0.90 and 1.11 eV are clearly resolved for samples grown at substrate temperatures from 500 to 580 °C. Since the relative intensities of these lines vary strongly even for samples grown under similar conditions, we conclude that the three PL lines originate from different defects or impurities. While the origin of the lines at 1.11 and 0.88 eV is yet not clear, we have strong evidence that the peak at 0.90 eV stems from the so called rod-like (or {311}-) defect (RLD) which will be discussed below. RLDs are agglomerations of Si self-interstitials. A detailed microscopic model can be found in [3]. It was reported that such RLDs are correlated with a PL line at 0.903 eV [4].

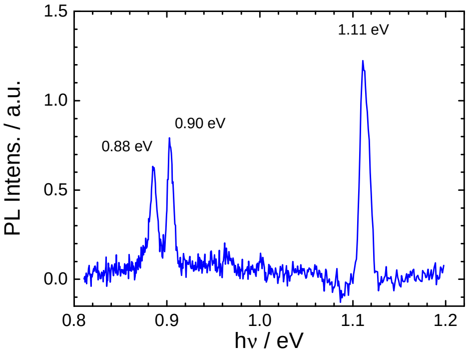

Figure 5: PL Spectrum of an epitaxial layer. PL lines are seen at 0.88, 0.90 and 1.11 eV.

3.5 Etch experiments

In order to test whether the PL peak at 0.9 eV observed in our samples is also related to RLDs we performed defect etching experiments using a Secco etch. With this technique, structural defects can be visualized, because the Secco etch preferentially etches the distorted regions around such defects.

For our samples the etching resulted in several distinguishable etch structures. The existence of one elliptical etch pit as shown in the SEM micrograph presented in figures 6a and b clearly correlates with the appearance of the PL peak at 0.90 eV. The directions of these etch pits are similar to what is predicted for RLDs as sketched in Fig. 7. Such RLDs are oriented along the <110> directions forming a 45° angle with the (100) surface as also shown in Fig. 7. Comparing this with the SEM images of the elliptical etch pits in figures 6a and b shows that this observation is in good agreement with the proposed model for RLDs. Thus we arrive at the conclusion that the PL peak at 0.90 eV and the elliptical etch pits stem from RLDs.

4 DISCUSSION

Results of HE and CV measurements at RT agree well within the experimental accuracy. We found that electron concentrations at RT are more or less insensitive to temperature variations during growth and are well above the total concentration of the deep levels. In addition, n(T) curves taken down to 30 K, which were not shown here, reveal a similar behavior as n(T) curves of Si wafers doped with the well understood shallow P donor. Although we could not determine the thermal activation energy exactly, this indicates that the dominant donor is shallow with an energetic distance to the lower conduction band edge well below 100 meV. This agrees with details of the ESR spectra of the dd resonance, which apparently stems from the dominant shallow donor in its occupied (neutral) state.

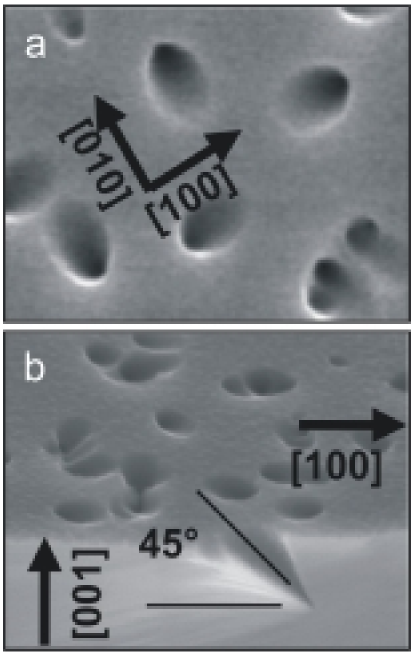

Figure 6: SEM pictures of elliptical etch pits. a) Top view (along the [00-1] direction). b) Side view (approximately along the [010] direction).

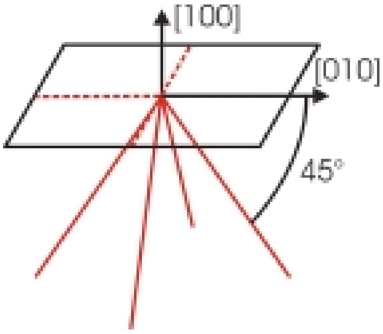

Figure 7: Sketch of the extension of the rod-like defects (RLDs) as indicated by the solid line.

DLTFS spectra on numerous samples showed that L2 is the dominant deep level at E_C - 0.28 eV with a broadened line shape the origin of which is still unknown. A possible cause of such a broadening is the presence of extended defects [5]. The results of the Secco etch experiments seem to support this idea. Further investigations are still necessary to clarify this point.

The db line observed in the ESR spectra have a similar g value as the well-known dangling bond lines observed in amorphous and microcrystalline silicon [6], however the saturation behavior is clearly different. We believe that the db line in our material originates from dangling bond-like defects that are clustered, probably at extended defects. Hence there will be a strong spin-spin interaction that would explain both the line shape and the saturation behavior.

In PL only one of the three, namely that at 0.9 eV can be assigned to defect previously reported in the literature. The PL peak correlates well with the appearance of elliptical etch pits that were identified to have a symmetry that corresponds to RLDs.

5 SUMMARY

N-type conductivity is observed in our nominally undoped epitaxial Si layers grown at temperatures below 600 °C. A shallow donor near the conduction band edge is the main cause. In its neutral state, the donor generates an ESR signal with $g = 1.999$. Several deep levels in the upper part of the forbidden gap are found with concentrations in the 10^{13} - 10^{15} cm^{-3} range. The dominant line at E_C - 0.28 eV reveals a broadened line shape, which could be related to the presence of extended defects. The latter were observed in etch experiments directly. The well-known rod-like defects and the related PL line at 0.90 eV were detected.

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