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Annealing Studies of the Microcrystalline Silicon System

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ABSTRACT

Annealing studies on intrinsic and doped microcrystalline silicon prepared with low temperature PECVD reveal the significance of percolation processes in this material. Electrical transport and optical spectroscopy are used to investigate the effects of annealing on the structure and the transport properties of the material.

1. INTRODUCTION

The use of microcrystalline silicon (μc-Si:H) layers in thin film devices requires a careful optimization and understanding of the electronic properties of this material. At present even one of the most fundamental properties - the temperature dependence of the dark conductivity - is still not understood. In various reports on conductivity of μc-Si:H, usually covering only a small temperature range, a thermally activated transport process with well defined activation energies [1] has been proposed. Previously, we pointed out that a simple activated behaviour for the electrical transport is not found when a wide temperature range is covered [2]. Therefore transport in μc-Si:H can not be interpreted in terms of an activated transport across grain boundary potential barriers with well defined activation energies. Instead we have to anticipate the complex structure of μc-Si:H which should be treated as a composite material of (1) crystalline grains, (2) grain boundaries and (3) amorphous tissue, where the volume fraction of each constituent can vary and is strongly dependent on the preparation conditions. Correspondingly, the transport properties will depend on changes in the material "fine" structure. Additional effects are to be expected from the fact that typically the dimensions of the grains are of the order of only 100 Å. This again will have consequences on the electronic band structure and on the transport behaviour.

To investigate the transport properties of microcrystalline silicon, we performed annealing studies in order to modify in a controlled manner the three phases of the composite material. It is known that hydrogen begins to evolve from μc-Si:H already near the deposition temperature [3,4]. Four dominant effects are to be expected from annealing: (1) defect creation through Si-H bond rupture, (2) defect/bond reconstruction, (3) dopant activation in the crystallites in doped material and (4) crystallization.

2. EXPERIMENTAL DETAILS

Samples were prepared with PECVD (70 MHz) from silane (1.5%) diluted in hydrogen with diborane and phosphine as dopant gases. Nominally intrinsic, highly conductive n- and p- type material and material prepared at 4.5% silane concentration close to the transition zone of amorphous to microcrystalline formation was investigated. Substrate temperatures were between 160 and 200 °C. Sample thicknesses were in the range 0.3 - 0.4 μm. Samples were annealed between the deposition temperature and 700 °C under high vacuum for about 30 min. For each annealing temperature Raman scattering (514.5 nm Ar-Laser, 100 mW, scanning mode), electrical transport (80 - 300 K), optical absorption (0.5 - 3.0 eV) and Hall effect was measured. Electrical transport was measured with contacts in van der Pauw geometry to minimize effects from contact resistances.

3. RESULTS AND DISCUSSION

Fig. 1 shows the Raman spectra for the sample A at two annealing temperatures. The sample was prepared with 4.5% silane close to the critical threshold for microcrystalline formation. The Raman signal at 480 cm^{-1} suggests an almost complete amorphous phase which remains up

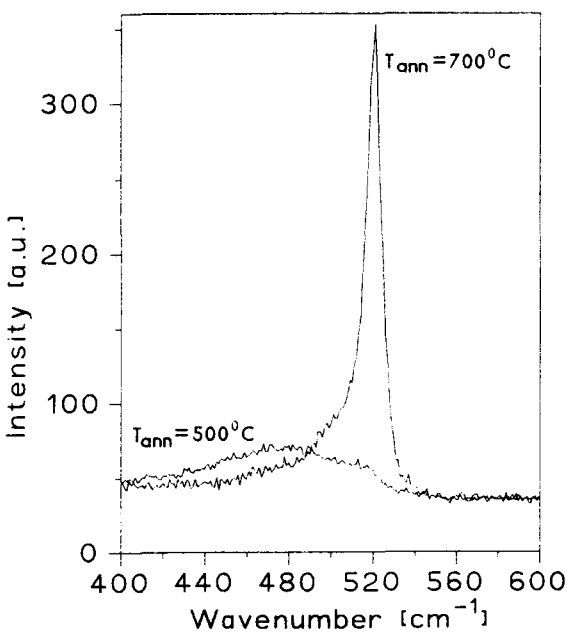

FIGURE 1: Raman spectra of sample A at two annealing temperatures.

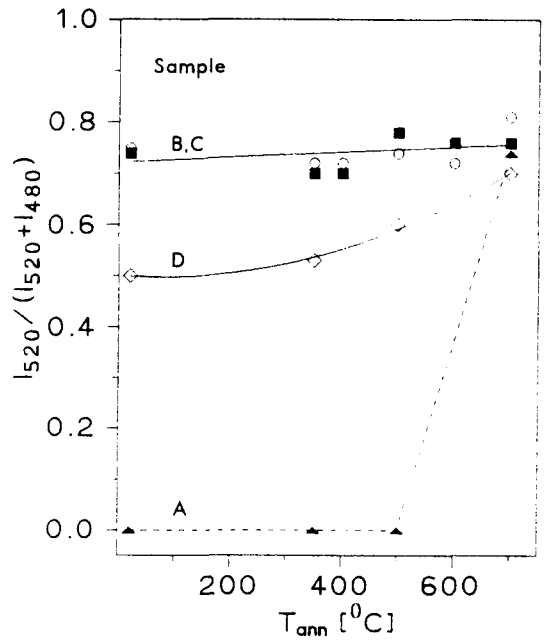

FIGURE 2: Intensity ratio of Raman lines vs. annealing temperatures.

to annealing temperatures of 500 °C. Strong crystallization is indicated only after annealing at 700 °C by a signal at 520 cm^{-1}. A quantitative determination of the volume fractions depends on the ratio y of the Raman scattering cross section of the crystalline and amorphous phases. This value is still controversial and probably varies with grain size [5,6]. We therefore only use the integrated intensities (y=1) of the line contributions at 480 and 520 cm^{-1} as a qualitative measure of the volume fraction. The results for all samples are summarized in Fig. 2 where the ratio of the integrated intensities of the Raman lines is plotted vs. annealing temperatures. We note that the highly conductive n-type and nominally intrinsic μc-Si:H (Samples B and C) show only small changes in the ratio of crystalline to amorphous phase with annealing as indicated by a constant intensity ratio around 0.75. In the highly conductive p-type material (Sample D) the intensity ratio increases from 0.5 in the as deposited state to 0.7 at T=700 °C. An annealing temperature of 700 °C should result in complete crystallization; therefore the intensity ratio of 0.75 could in fact be considered to correspond to a crystalline volume fraction close to 100%.

Next we turn to the temperature dependence of the dark conductivity σ_D. As a function of temperature, the electrical conductivity shows a strong deviation from a simple activated behaviour for all samples at all annealing stages. In Fig. 3 we show as a representative example the dark conductivity σ_D for sample A after various annealing steps in a plot of σ_D vs. $10^3/T$. Sample A was identified as "amorphous" in the as-deposited state from the Raman signal. However, the high conductivity in the as-deposited state is not typical for phosphorus doped a-Si:H (conductivities for the highest doping levels in a-Si:H do not go beyond 10^{-2} S/cm). Whereas little changes in the conductivity are observed up to annealing temperatures of 500 °C, a sudden increase is observed at T=700 °C in correspondance with the structural changes indicated by the Raman spectra. Note also that the characteristic shape of the conductivity curves does not change.

The RT-transport data for all samples are summarized in Fig. 4. Sample B (highly conductive n-type) shows only small changes in σ_D with annealing similar to the small changes in the Raman intensity ratio that remains around 0.75. In contrast sample C - the nominally intrinsic sample that also had a high initial volume fraction of crystallites - shows the most profound changes in conductivity. The RT conductivity decreases by 5 orders of magnitude after annealing at temperatures above 350 °C and then increases at the final annealing stage. The initial decrease can be explained by a compensation effect. The nominally undoped sample is n-type through residual gas

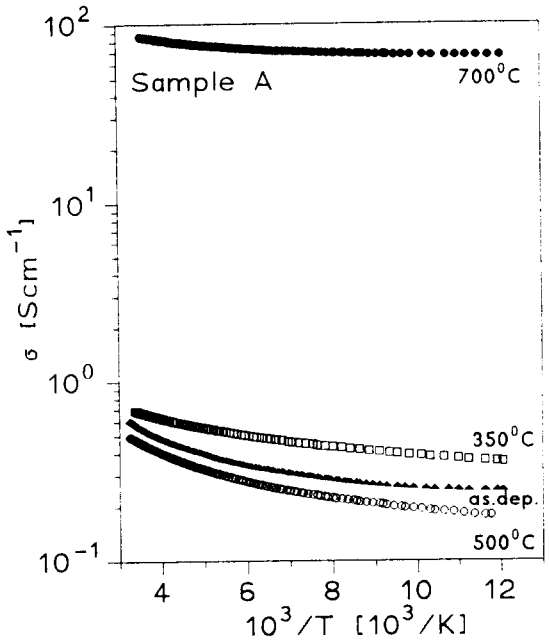

FIGURE 3: Dark conductivity of sample A vs. $10^3/T$ at different annealing steps.

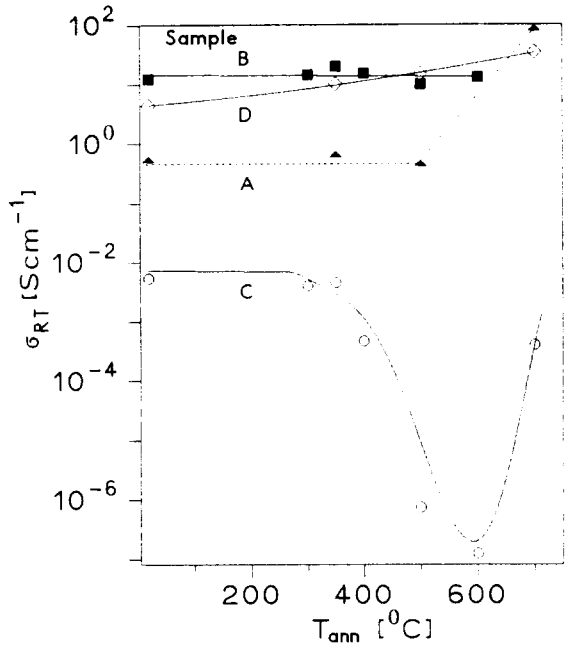

FIGURE 4: Room temperature conductivity vs. annealing temperature for all samples.

doping. The sample was prepared in a chamber used for heavy phosphorus doping. Upon annealing defect states are created at the grain boundaries through Si-H bond rupture and H diffusion along the grain boundaries. These defect states trap free carriers at the grain boundaries leading to a decrease in conductivity. At the highest annealing temperature bond reconstruction occurs, reactivating free carriers.

This effect should also be present in the highly doped samples. However, here it is counterbalanced by two other processes: first the initial free carrier densities are much higher and second annealing allows H to break from passivated dopants (P-H and B-H) in the crystallites and make them active. This latter effect already occurs at annealing temperatures near the deposition temperature [3,4]. Finally, for sample D (highly conductive p-type), which had a volume fraction of about 50% in the as-deposited state, the increase in conductivity follows nicely the increase in crystallinity as exhibited by the Raman data.

The structural changes due to hydrogen effusion and crystallization are also seen from the optical absorption spectra (not shown). For samples A and D which show increases in crystallinity, the slope of the optical absorption edge decreases at the highest annealing temperature - a typical feature of the microcrystalline phase with respect to the amorphous phase. The samples showing no or little change in crystallinity instead only show a red shift of the absorption edge. The latter effect is observed for all samples in the initial annealing steps and can be explained by the removal of Si-H bonds from the grain boundaries or the amorphous tissue which is known to cause a red shift in the absorption.

The carrier density measured by the Hall effect follows the conductivity of the samples. Annealing mainly affects the carrier density through dopant activation and crystallization (dopants are much less active in the amorphous network).

With regard to structure the samples investigated here fall into three categories:

(1) samples B and C with a high, almost complete degree of crystallinity in the as-deposited state where annealing has little or no influence on the structural properties seen by Raman,

(2) sample D with considerable amorphous tissue remaining in the as-deposited state,

(3) sample A which seems Raman-amorphous but indicates microcrystalline transport mechanisms.

Samples of class (1) represent the optimum material quality resulting from the low temperature PECVD process used here. Crystallinity can not be improved by annealing and crystallite sizes seem to be unaffected. The high crystallinity implies that transport should be dominated by transport through percolation paths made of crystalline material

(theoretical and experimental work predicts a percolation threshold below 20% crystalline volume fraction [5,7]). Generally, grain boundaries along the percolation paths act as potential barriers that affect the mobility. Because of a wide distribution in grain sizes one would also have a distribution in barrier heights with the possibility of transport channels with very small potential barriers and high mobilities. This is true in particular for highly doped material.

In a simple two path model [8], the mobility μ is given as

$$\mu = \Sigma \mu_i f_i$$

with two carrier paths with high and low mobility, respectively. f_1 and μ_1 correspond to the high mobility path (percolation), and f_2 and μ_2 to the low mobility path across potential barriers. f_1 is much smaller than f_2. This means at low temperatures transport is dominated by percolation, whereas at high T activation across barriers (because of the large number of these paths) becomes dominant. This approach explains qualitatively the curvature of the σ_D vs. 1/T curve.

In class (2) the material is strongly affected by boron doping. It has been reported that boron hinders crystalline growth in PECVD processes [9]. Here further optimization of the process is required. Percolation still plays a dominant role in the transport process. We see that after annealing and a considerable increase in crystallinity the characteristic shape of the σ_D vs. 1/T curve does not change, but only shifts to higher σ_D-values. It appears as if additional transport paths of the same type are opened up while no changes in the dominant transport mechanisms are observed.

Class (3) finally represents material prepared close to the transition zone between amorphous and microcrystalline formation i.e. close to the critical silane to hydrogen ratio. This material seems amorphous in Raman spectra but the transport data suggest that microcrystalline current paths could be present. Indeed, most recent TEM measurements on this sample confirm the presence of microcrystallites with low concentration and sizes. Here a considerable increase in the crystalline volume fraction occurs only above the crystallization temperature.

4. CONCLUSION

Microcrystalline silicon prepared with low temperature PECVD and a wide range of crystalline volume fractions shows a strong indication for electrical transport through percolation paths. These transport paths dominate the conductivity behaviour, particularly for highly doped material. Only at high temperatures and for samples with the Fermi level position near midgap do thermally activated processes play a major role.

5. ACKNOWLEDGEMENT

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REFERENCES

[1] for a recent overview see: Mat. Res. Soc. Symp. Proc. **283** "Microcrystalline Semiconductors: Materials Science & Devices", 1992

[2] F. Finger, R. Carius, P. Hapke, K. Prasad and R. Flückiger in ref.[1] p. 471

[3] F. Finger, K. Prasad, S. Dubail, A. Shah, X.-M. Tang, J. Weber and W. Beyer, Mat Res. Soc. Symp. Proc. **219** (1991) 469

[4] K. Prasad, F. Finger, S. Dubail, A. Shah and M. Schubert, J. Non-Cryst. Solids **137&138** (1991) 681

[5] R. Tsu, J. Gonzalez-Hernandez, S.S. Chao, S.C. Lee and K. Tanaka, Appl. Phys. Lett. **40** (1982) 534

[6] E. Bustarret, M. A. Hachicha and M. Brunel, Appl. Phys. Lett. **52** (1988) 1675

[7] H. Scher and R. Zallen, J. Chem. Phys. **53** (1970) 3759

[8] M. Nakata and I. Shimizu in ref. [1] p. 591

[9] K. Prasad, U. Kroll, F. Finger, A. Shah, J.-L. Dorier, A. Howling J. Baumann and M. Schubert, Mat Res. Soc. Symp. Proc. **219** (1991) 383