TRANSPORT PROPERTIES OF SILICON LAYERS GROWN BY LIQUID PHASE EPITAXY (LPE) FOR PHOTOVOLTAIC APPLICATIONS

R. Kopecek, J. Hötzel, S. Volz, K. Peter, E. Bucher
Universität Konstanz, Fachbereich Physik, Fach X916, 78457 Konstanz
Tel.: +49-7531-88-3174, Fax: +49-7531-88-3895
E-mail: radovan.kopecek@uni-konstanz.de

ABSTRACT: This paper describes the growth of Si layers on monocrystalline highly resistive boron doped (100)-oriented FZ substrates from an In/Ga respectively Sn/Ga solution for parametric studies. All processed LPE layers were grown in an In(6N)/Ga and two Sn/Ga solutions of different purity (3N resp. 5N) saturated with Si at temperatures around 920°C in a resistively heated furnace. The relatively high temperature guaranteed the complete removal of the remaining oxide on the substrate surface, hence a smooth and uninterrupted growth of the thin layer. For the optimisation of layer properties for solar cell applications, parameters such as initial temperature, growth rate and Ga concentration of the In respectively Sn solutions were varied.

Hall measurements, X-ray spectroscopy, mechanical surface profiling (Dektak) and a lifetime analyser were used to characterise the 100-200 µm thick LPE layers. In order to obtain their structural and electrical transport properties the layers were grown preferably on monocrystalline highly resistive boron doped (100)-oriented float zone (FZ) substrates. This fact enabled uncomplicated and fast characterisations without having to remove the grown LPE layer from the substrate.

The parameters obtained for high quality layers are applied to layers grown on polycrystalline metallurgical grade (MG) silicon substrates for the fabrication of inexpensive solar cells.

Keywords: LPE - 1: Thin Film - 2: Characterisation - 3

1. INTRODUCTION

Thin silicon layers on inexpensive heavily doped polycrystalline Si substrates offer a promising alternative to conventional bulk material used for solar cells. The main reason for experiments conducted with such thin layers of 10-50 µm thickness is the immense reduction of Si consumption which still represents about one third of the costs of a complete module. The method of LPE is a good alternative to chemical vapour deposition (CVD) for growing thin Si layers of high quality. The comparison of the structural and electrical properties of polycrystalline Si layers grown by CVD and LPE on multicrystalline substrates with similar grain boundary structures show the electrical quality of LPE samples to be significantly better than those of the CVD samples [1]. Thin layers with previously optimised electrical transport and structural properties grown for example on polycrystalline metallurgical grade (MG) silicon substrates can be used for the fabrication of inexpensive solar cells.

2. EXPERIMENTAL SETUP AND EPITAXIAL GROWTH

All layers were processed in a resistively heated LPE furnace of which Figure 1 shows the most important parts. It consists of a cylindrical quartz tube surrounded by two separately controllable coil heaters. The temperature is measured by two thermocouples in the furnace outside the quartz tube and is controlled by a PC. The quartz crucible in the tube is filled with the solvent saturated with Si at around 920°C. At one end of the tube the substrates are loaded through a lock which can be evacuated or filled with H_2 protective gas. The loaded substrate is attached to a holder on a quartz rod. It is driven over the solution and is

placed onto the surface so that only one side is covered. During the process the quartz tube is swept by pure hydrogen (5N) which is additionally purified by a palladium filter. Conventional LPE crystal growth relies on continuously flowing purified hydrogen into the system to avoid oxide formation on the substrate surface [2,3].
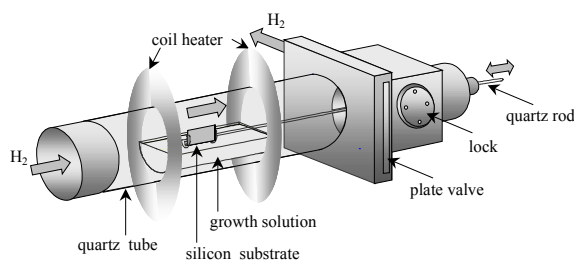

Fig. 1: LPE furnace.

In order to minimise the effect of the substrate in the electrical measurements, the LPE layers were grown on monocrystalline boron doped (100)-oriented FZ silicon substrates with a resistivity above 2 kΩcm. The substrate size amounted to 25·50 mm². Prior to layer growth the substrates were prepared by etching in a NaOH solution to remove saw damage. After this step they were oxidised in H_2O_2:H_2SO_4 (1:4) for ten minutes. Before entering the furnace the covering oxide was removed with a dip in a 2% HF solution. In the furnace the substrates were placed onto the surface of the metal solution at approximately 920°C. This relatively high temperature guarantees the removal of the remaining oxide and therefore an uninterrupted and smooth growth of the thin layer. The growth rates were varied between 2 and 90 µm/h.

3. MEASUREMENT OF ELECTRICAL TRANSPORT PROPERTIES

Hall measurements were performed to examine the electrical transport properties of the LPE layers. The Hall coefficient R_H and the resistivity ρ were measured between 30 and 450 K. Low temperatures were achieved by pumping expanded helium gas through the sample chamber. The sample temperature was measured by a thermocouple mounted in the sample chamber, a few millimetres from the sample. Ohmic contacts were achieved by the diffusion of an aluminium paste for p-conducting and a silver paste for n-conducting layers (usually used for the screen printing process of the solar cell back and front contacts respectively) for 30 minutes in a forming gas atmosphere at 700°C. Electrical contacts to the sample were made via gold wires fixed to the diffused contacts by a silver epoxy paste.

The resistivity of the 500 μm boron doped substrate is higher than 2000 Ωcm. Theoretical calculations and experimental results yield that in the region of room temperature the influence of the substrate during the measurement is negligible.
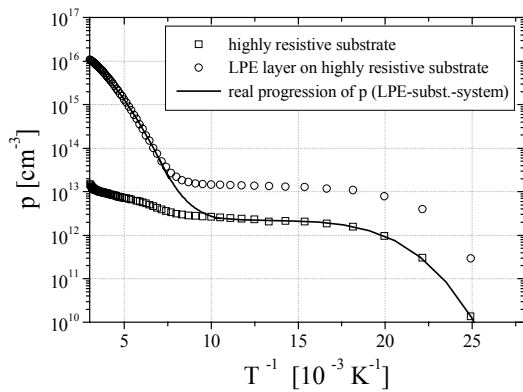

Fig. 2: Temperature dependent carrier concentration of the highly resistive substrate and of the LPE layer grown on this substrate from a pure In solution.

Figure 2 shows the temperature dependent carrier concentration of the highly resistive substrate and of the LPE layer grown on the substrate from a pure In solution. At low temperatures the carrier concentration p increases with temperature because of the low activation energy of boron ($E_{A,\ boron}$ = 45 meV). At temperatures around 60 K almost all boron acceptor levels are saturated and the carrier concentrations have a constant value of $p=2\cdot10^{12}$ and $p=1\cdot10^{13}$ cm^{-3} respectively. At 140 K the carrier concentration of the LPE layer increases due to the activation of the indium acceptor levels. Indium has an activation energy of $E_{A,\ indium}$ = 156 meV [4], which is four times higher than that of boron. The difference between the carrier concentrations of the two measurements at temperatures below 140 K can be explained by the unequal thickness of the relevant layers ($d_{LPE} \approx 100$ μm, $d_{subst.} \approx 500$ μm). Therefore the concentration in the twofold system seems to be about 5 times higher than in the simple case. The solid line in Fig. 2 hence represents the real temperature dependent progression of the carrier concentration p. If the relevant temperature range is above 140 K then this arrangement provides an easy method for Hall measurements without requiring the separation of the substrate. An additional advantage is the possibility of an adjusted temperature gradient in the furnace allowing the growth of wedge shaped layers on a plane substrate. This in turn enables the preparation of Hall samples with different growth rates out of one single grown layer.

The use of highly resistive substrates also enables the precise lifetime measurements of the minority carriers. During the measurement a short laser pulse of 160 ns with a wavelength of 904 nm creates electron hole pairs. The recombination after the pulse is detected via micro wave (μ-wave) reflection.
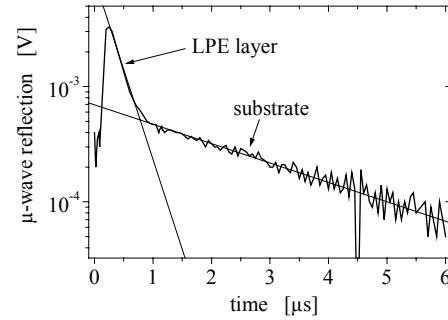

Fig. 3: Typical lifetime measurement of an LPE layer grown on a highly resistive substrate. The different lifetimes of the analysed layers result in the bi-exponential decay of the microwave signal.

Figure 3 shows a lifetime measurement of an LPE layer grown on a highly resistive substrate for a single laser spot. The faster decay with a steeper decline results from the LPE layer, whereas the slower decay from the substrate itself. In order to measure the lifetime of the LPE layer and the substrate both parts were fitted with a mono-exponential curve $I \propto \exp(-t/\tau_n)$. To examine the whole layer the surface was scanned using a laser beam with a diameter of less than 1 mm.

4. STRUCTURAL AND ELECTRICAL LPE LAYER PROPERTIES

4.1 Dependence on growth rate

For photovoltaic applications the material must have a sufficiently smooth surface in order to guarantee a good deposition of finger contacts allowing current flow without interruption. The roughness of the layer surface can be considerably reduced if the layer is deposited with a small growth rate and if a low Ga concentration is used in the solvent [5].

X-ray photoluminescence measurements indicated higher segregations of the doping atoms from the solution into the LPE layer with the increase of growth rates. Corresponding Hall measurements on the other hand showed an almost constant carrier concentration and a decreasing Hall mobility. This observation can be explained by the fact that the high segregation of In atoms into the LPE layer at high growth rates occurs without the development of an acceptor level. Such segregated In atoms are inactive in the LPE layer and do not contribute to the conductance. They simply serve as scattering centres and increase the resistance of the material [5].

4.2 Dependence on Ga concentration in the solution

The properties of the LPE layers can be altered by their growth in different solutions. Three different solutions were used – an In solution (6N) and two Sn solutions of different purity (3N and 5N). The concentration of Ga in these solutions was chosen as 0, 0.1 and approx. 1 weight% (for In also 23 weight% Ga). In each solution the layers were grown under the same conditions and examined by Hall measurements. The results of these measurements are depicted in Figure 4.
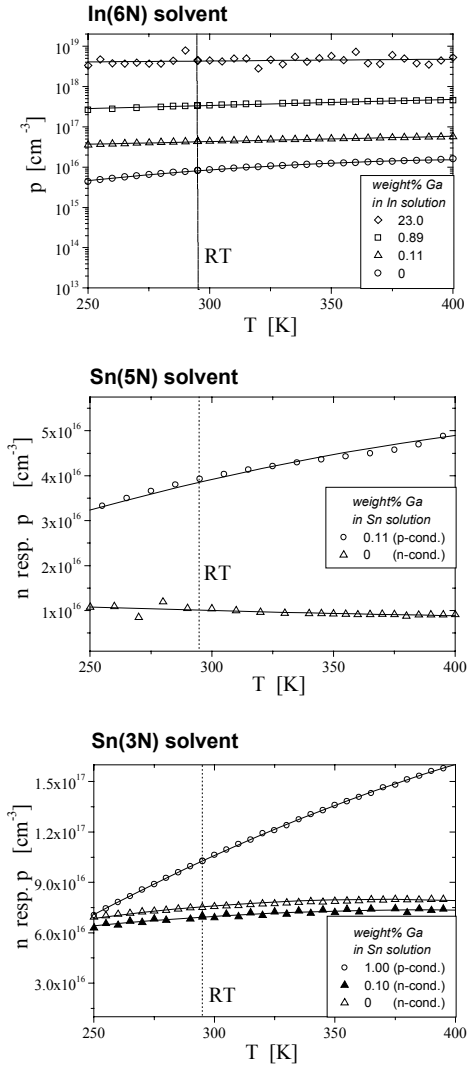

Fig. 4: Temperature dependent carrier concentrations n resp. p of LPE layers grown from different solutions.

It shows the temperature dependent carrier concentrations of the LPE layers grown from different solutions. Layers grown from a pure In solution are p-conductive and the hole concentration p increases with increasing Ga concentration. The growth initiated from a pure Sn solution leads to n-conducting layers. This n-conducting character can be explained by the segregation of impurities such as Sb and Bi into the LPE layer. This assumption is confirmed by the fact that the electron concentration depends on the purity of the solvent. Layers grown from 5N Sn have an electron concentration of

$1.1 \cdot 10^{16} cm^{-3}$ compared to an almost ten times higher concentration for 3N Sn. Adding Ga to the Sn solution leads to the segregation of Ga atoms into the LPE layer and thus to the compensation of the conducting electrons. The transition to a p-conductive state for layers grown from the 5N Sn solution already occurs with the addition of just 0.11weight% Ga. Due to the higher concentration of Sb and Bi in the 3N Sn solution the layers will not become p-conductive without the addition of 1 weight% Ga. The electrical transport properties for a representative selection of the processed LPE layers are summarised in Table I.

Tab. I: Electrical transport properties at room temperature of the LPE layers processed on highly resistive substrates.

ID Nr.	Solvent/ dopant	Cond. type	Doping $[cm^{-3}]$	Mobility $[cm^2/Vs]$	Cond. $[\Omega cm]$
P6	**In (6N)**	p	$1.0 \cdot 10^{16}$	233.8	0.39
R8	In / 0.11w% Ga	p	$4.0 \cdot 10^{16}$	207.0	1.34
S7	In / 0.89w% Ga	p	$7.2 \cdot 10^{17}$	119.9	13.8
Z2	In / 23.0w% Ga	p	$4.3 \cdot 10^{18}$	27.2	20.0
α1	**Sn (5N)**	n	$1.1 \cdot 10^{16}$	1293.0	1.69
α8	Sn / 0.11w%Ga	p	$3.9 \cdot 10^{16}$	101.1	0.64
Y2	**Sn (3N)**	n	$9.3 \cdot 10^{16}$	294.4	4.35
Y10	Sn / 0.12w% Ga	n	$7.0 \cdot 10^{16}$	210.0	2.38
Y16	Sn / 1.0w%Ga	p	$1.0 \cdot 10^{17}$	65.5	1.08

The hatched rows correspond to layers which are suitable for conventional photovoltaic applications (p ≈ $4 \cdot 10^{16}$-10^{17} cm^{-3}). The hole mobility of the layers grown from both Sn solutions is lower because of their lower purity leading to an additional segregation of n endowing impurities into the layer such as As, Sb and Bi.

5. SOLAR CELLS ON MG SUBSTRATES

Based on these parameters thin layers of 30-100 μm thickness were grown on metallurgical grade (MG) substrates and solar cells were processed with a low cost method. The obtained cell parameters are shown in Table II.

Tab. II: Results of low cost solar cells processed on thin layers grown on MG substrates with the LPE method from different solutions (6N In, 5N Sn, 6N Ga).

Sub.	Solut.	A $[cm^2]$	Voc $[mV]$	Isc $[mA]$	FF $[\%]$	η $[\%]$
1/3 MG	In+Ga	3	534.3	26.3	63.3	9.0
MG	In+Ga	2.2	560.2	25.2	56.9	8.0
MG	Sn+Ga	3.6	492.7	22.1	52.4	5.7

The cell with the highest efficiency of 9.9% was processed out of an LPE layer grown from an In/Ga solution on a MG substrate in Freiburg at the FhG-ISE and therefore does not figure in the above table. The highest efficiency effectuated for cells on an LPE layer grown on a highly doped mc substrate was 11.6%, on a highly doped CZ substrate even 15.0%.

Simulations with PC1D show that cell efficiencies around 12% should be feasible on LPE layers grown on MG material using either an In or a Sn solution. A possible

reason for all cell efficiencies remaining below 10% is the diffusion of the impurities (Ca, Al, Fe, Ni, Cr) from the MG substrate into the LPE layer. SIMS measurements indicated Ca atoms in the LPE layer with a concentration of about 10^{17} cm^{-3}. All other impurities were determined to be less than 0.1 ppma. The main reason for the low efficiencies is probably a short circuit of the cells and therefore the macroscopic quality of the LPE layer. SEM pictures sometimes show small interruptions in the layer. To improve the character of the layers higher growth temperatures above 1000°C will be used in future experiments. On the one hand the diffusion of impurities into the LPE layer will increase (e.g. for Fe by a factor of 4 at 1100°C) but on the other hand smoother and more continuous layers can be expected which could lead to higher efficiencies.

6.   CONCLUSION

We have demonstrated the epitaxial growth of Si LPE layers on monocrystalline highly resistive boron doped (100)-oriented FZ Si substrates in different solvents. Hall and lifetime measurements on such LPE layers grown on highly resistive substrates provide an easy and rapid characterisation method for the electrical transport properties.

The quality of the thin layers is very sensitive to the growth rate of the layers and to the Ga concentration of the solutions. Even surfaces of the thin film require very small growth rates and a low Ga content in the solution. With higher growth rates the segregation of the doping atoms from the solution into the LPE layer increases. Corresponding Hall measurements on the other hand showed an almost constant carrier concentration and a decreasing Hall mobility. This observation can be explained by the fact that the high segregation of the doping atoms into the LPE layer at high growth rates occurs without the development of an acceptor level. In order to obtain layers with good electrical properties low growth rates should be applied.

The ideal carrier concentration of the epitaxial layer for thin film solar cell applications (p = $4 \cdot 10^{16}$-10^{17} cm^{-3}) is obtained by the addition of 0.1 weight% Ga to the pure solution (6N In, 5N Sn) or 1.0 weight% to the 3N Sn solution at 920°C.

Solar cells were processed from LPE layers grown on MG substrates from different solutions with a low cost process. The cell with the highest efficiency (8.0%) was grown from an In/Ga solution. Solar cells with efficiencies of up to 9.9% from LPE layers grown on MG substrates were processed in Freiburg at the FhG-ISE. The results are published elsewhere at this conference.

In order to reach higher efficiencies the macroscopic quality of the thin layers must be improved. This can be attained by growth at higher temperatures leading to more homogeneous layers. Growth at temperatures above 1000°C shall be performed from a Sn solution, as In has approx. a 5 times higher vapour pressure than Sn.

In addition an alternative processing method for n-type base solar cells shall be pursued. The layers are to be grown from a pure 5N Sn solution at temperatures above 1000°C on previously phosphorus diffused MG substrates or other inexpensive n-type substrates (n-MG or n-RGS). The P diffused area prevents the undesirable formation of a diode between the substrate and the LPE layer and additionally serves as a back surface field (BSF) for the solar cell. One of the advantages of this alternative process

is the use of the cheaper Sn solution and furthermore a simpler cell processing method with only an inexpensive Al (or B) paste for the emitter diffusion, the front and the back contacts.

LITERATURE

[1] G. Wagner, H. Wawra, W. Dorsch, M. Albrecht, R. Krome, H. P. Strunk, S. Riedel, H. J. Möller and Appel, Journal of Crystal Growth, **174**, (1997), 680-685

[2] B. J. Baliga, Journal of Electrochemical Society , **133**, (1986) 1

[3] E. Bauser and H. P. Strunk, Mater. Res. Soc. Symp. Proc. , **37**, (1991) 339

[4] G. F. Cerofolini, L. Meda, Physical Chemistry of, in and on Silicon, Springer, Berlin (1989) 42-45

[5] R. Kopecek, K. Peter, J. Hötzel, E. Bucher, Journal of Crystal Growth, **208**, (2000) 289-296