THIN FILM SILICON FOR SOLAR CELL APPLICATION GROWN FROM LIQUID PHASE ON METALLURGICAL GRADE SILICON

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ABSTRACT: Liquid phase epitaxy was applied to grow roughly 10 µm thick n-type polycrystalline silicon film on p-type metallurgical grade (MG) silicon substrate at 900° C in gallium/indium solution. GaAs, dissolved in the melt, served as an arsenic donor source for the as-grown film. The carrier concentration of both the substrate and the as-grown film was 1×10^{18} cm^{-3} which is too high for practical photovoltaic applications. A post growth exposure to hydrogen plasma lowered the carrier concentration at the p-n junction by an order of magnitude, resulting in functional photovoltaic devices with an open circuit voltage V_{OC} of up to 480 mV. A morphology study, carried out by scanning electron microscope and atomic force microscope, revealed grain size in the range 1 – 3 mm, reflecting the grain size of the substrate. Our result indicates that usable solar-cells may be prepared from unmodified MG silicon without the costly need of recrystallisation for purification.
Keywords: Silicon solar cell, liquid phase epitaxy, metallurgical grade silicon, hydrogen passivation

1 INTRODUCTION

High purity silicon is by far the most important raw material for solar production today. As the world market for Si solar cell shows significant annual growth, a shortage of silicon will seriously constrain further increment. The existing photovoltaic technology is material intensive, as it uses relatively thick (~ 300 µm) wafers of expensive ultra-pure silicon. In recent years, the focus has been on the economical side of the solar cells fabrication instead of improving their performance, which is already relatively close to their optimum. Most of the crystalline Si material merely acts as a mechanical support for the solar cell device with most of the optical absorption taking place in the upper 30 µm [1]. Therefore the tendency is towards reducing material costs by using thinner wafers and by using cheaper and lower performance starting material [2, 3].

Thin film technology has been applied to create shallow and sharp p-n junction for photovoltaic application. One of the advantages of thin cells is that smaller diffusion lengths can be tolerated to maintain the same short-circuit currents than in the conventional solar cells [4] since the light-generated carriers have a shorter pathway to the surface contacts.

Although Si is an indirect bandgap semiconductor and therefore a relatively poor light absorber, efficient solar cells with reasonable current can, in principle, be achieved even in thin layers of only few µm in thickness. When special care is taken to maximize optical confinement, active layer thicknesses as low as 1 µm could be sufficient to reach energy conversion up to 17% [5].

Liquid phase epitaxy (LPE) is an attractive technique for silicon film deposition due to the simplicity of its technology and a growth temperature well below the melting point of Si. Epitaxial crystal growth with LPE occurs close to the thermodynamic equilibrium and therefore produces high quality crystal layers with low density of structural defects and low recombination activity at grain boundaries. Traditionally, the LPE technique has not been suitable for large-scale production. However, recent modifications towards large volume production [6, 7] have made the LPE technique attractive as a cost effective method for solar-cell production. The possibility of growing thin layer on low quality inexpensive substrate is of particular interest and has the potential to greatly reduce the production cost. The LPE technique, however, suffers from small solubility of Si in the most common metallic melts and high solvent content in the deposite. Thin Si film has been grown successfully with LPE on various substrates for solar cell applications, such as single crystal; multicrystalline; upgraded MG-Si [7, 8, 9, 10], porous Si and ceramics and glass [2, 11].

One of the crucial problems in solar cells is that significant part of the incoming radiation is reflected, which limits the efficiency of such devices. Silicon based solar cells reflect approximately 30% of the incident light in the spectral range where Si is photosensitive [12]. Therefore the surfaces of crystalline silicon solar cells are usually textured to reduce the surface reflectance which may increase the efficiency considerably. In some cases, production of thin film for solar cell application might incorporate such a texture and thereby lower or exclude the need for additional anti-reflection treatment.

Carrier concentration of 5×10^{16} cm^{-3} − 10^{17} cm^{-3} has been considered suitable for photovoltaic application [13] which is less than one tenth of the value for MG-Si. Hydrogen is known to passivate both donors and acceptors in virtually all semiconductors and has been used effectively to reduce the defect concentration in polycrystalline silicon film by 10^{17} cm^{-3} to a sub-micron depth [14]. Here we grow Si thin film on un-modified MG-Si and use hydrogen plasma to passivate the carriers to suitable levels.

2 SAMPLE PREPARATION AND EXPERIMENT

A polycrystalline MG silicon substrate was obtained by cutting and polishing raw MG silicon chunks of grade 441 (0.40% wt of Fe and Al and 0.10% of Ca), into 0.5 mm wafers. The MG silicon chunks were supplied by Bit Metals BV. A conventional horizontal graphite sliding crucible system [15] was used for the growth experiments. To suppress oxide formation on the substrate surface, a continuous flow of reducing atmosphere of palladium purified H_2 was maintained during growth. As a growth solution, gallium and indium in the weight ratio of 3:1 and purity 6N and 4N respectively, were used. In that composition the alloy is close to its eutectic with a melting point of 25°C. Due to the trivalency of gallium, silicon grown from Ga melt results in very high doping level due to segregation of Ga atoms into the LPE layer [13] which means that the grown film automatically becomes p-type unless compensated by sufficient amount of donor dopant. Here, the desired film is n-type. Despite this contradiction the Ga/In solvent was chosen for several reasons: firstly, because of its low melting point which makes all post cleaning of samples and graphite crucibles much easier; secondly, because of its high silicon solubility when compared to other possible tetravalent solvents such as tin and indium and thirdly it was chosen to compromise the high solubility provided by Ga and the beneficial electrical properties provided by In [16]. A 4×10^{-2} wt. percent of undoped GaAs was dissolved in the melt serving as a donor dopant. This amount corresponds to roughly 0.03 atom % of As relative to the Ga amount. Prior to growth, the melt was nearly saturated with undoped silicon. This slight undersaturation served to provide a melt-back step and to remove native oxide layer from the substrate prior to growth. After stabilization of temperature at 900° C the substrate was pulled into the growth solution. After one hour at 900° C the temperature was gradually lowered with the rate of 2°C/min to 880° C. Deposition took place on both the upper and the lower side of the substrate. After being cooled to room temperature the samples were taken out of the furnace. A residual metal solvent was wiped off the samples with cotton-pins while immersed in warm methanol. After drying, the samples were cleaned in ultrasonic bath with $HCl:H_2O$ (1:10) solution for 10 minutes. The thicknesses of the as-grown films were estimated from the drop in solubility of silicon in Ga when lowering the growth temperature. Hall measurements were applied to determine the majority carrier concentration of the substrate and the LPE film. Using square samples in the van der Pauw configuration, ohmic contacts were welded on the four corners with gold wire. The Hall coefficient R_H was estimated from the slope of the Hall voltage versus magnetic field in the range of 0 – 0.50 T. The as-grown samples were exposed to H_2 /Ar_2 plasma in an inductively coupled discharge applied with a power of 80 W for 40 minutes. No external heating was applied to the samples. During the hydrogenation, the pressure was kept at 10 mTorr with partial argon pressure of 50%.

Keithley 615 ammeter was used to measure the current-voltage (I -V) characteristics. The open-circuit voltage, V_{OC}, was measured in samples of size 2 × 2 mm^2 with digital storage oscilloscope under illumination of pulsed red laser diode light. Several samples, taken from different positions of the as-grown area, were prepared. Topographical information was obtained by atomic force microscope (AFM) and scanning electron microscope (SEM).

3 RESULTS AND DISUSSION

The Hall carrier concentration was measured as $p = 1 \times 10^{18}$ cm^{-3}, both in the MG-Si substrate and the as-grown film prior to hydrogenation which is roughly an order of magnitude higher value than desired. The *I-V* characteristics of the p-n junction before and after hydrogenation are shown in figure 1. As clearly visible, the hydrogenation has a significant influence on the electrical properties.

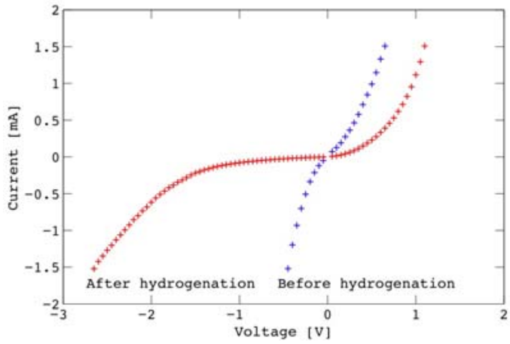

Figure 1: *I-V* characteristics of a diode grown with LPE on MG-Si before and after hydrogenation

Prior to hydrogenation almost no difference between forward- and reverse bias was seen and no photovoltaic response was observed during illumination with the red light source. After hydrogenation the *I-V* curve resembles more a diode-like behavior and the open circuit voltage V_{OC} was measured in the range of several tens of mV to a peak value of 480 mV under the same experimental conditions. Such a large variation in the voltage could be explained by structural imperfections in the MG-Si substrate, which consequently leads to an inhomogeneous film. The peak value of 480 mV does however indicate that hydrogen is able to passivate interface states at the p-n junction at the depth of several µm which is deeper than normally observed. This may be attributed to grain boundary diffusion in the polycrystalline film.

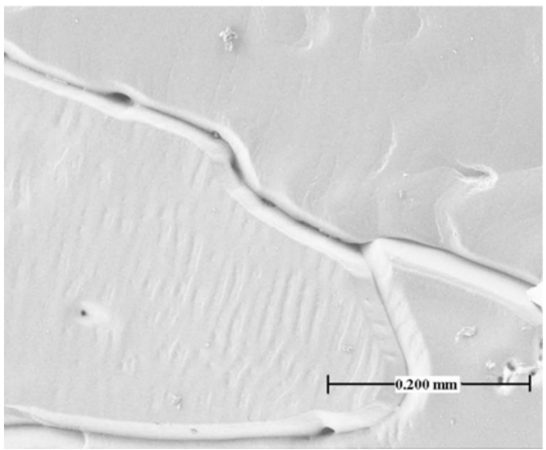

Figure 2: SEM micrograph of Si grown in Ga/In solvent on MG-silicon substrate at 900°C.

In the SEM micrograph in figure 2, cross sections of grains of the order of few mm^2 in size are seen. The wide boundaries between the grains are clearly visible. The reason is that non-crystalline silicon at the grain boundaries of the substrate is dissolved at much faster rate than the crystalline parts of the grains during the melt-back step. Growth does not occur in these depleted areas and consequently, channels for hydrogen migration are left open. A porous nature of the substrate could also be a part of the explanation.

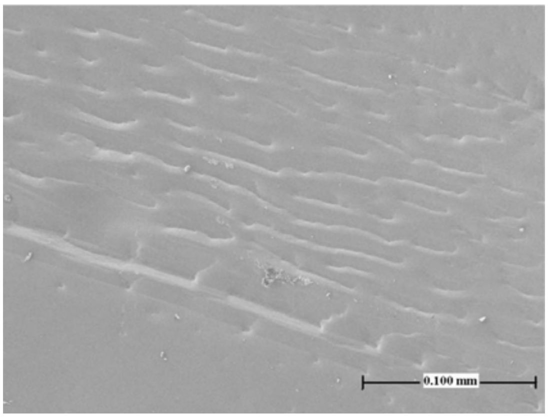

Figure 3: SEM micrographs of Si grown in Ga/In solvent on MG-silicon substrate at 900°C

Figure 3 depicts the relatively flat surface of the film. Contour of the film over an area of 40 × 40 μm^2 is shown in figure 3, giving the RMS roughness as approximately 30 nm. A value of roughness closer to the wavelength of visible light would have been desired in order for the fraction of reflectance to be low. Thus, an additional texturing process might be required for practical applications.

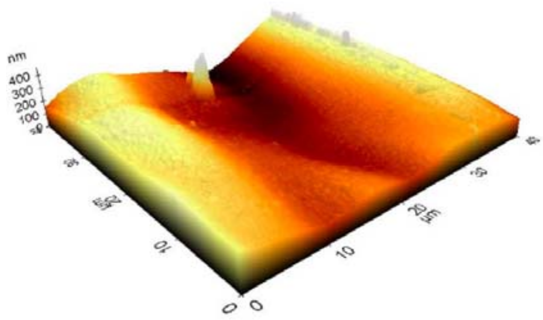

Figure 4: AFM micrographs of Si grown in Ga/In solvent on MG-silicon substrate at 900°C

4 CONCLUSION

A p-n junction in silicon was prepared by growing thin n-type film on un-modified MG-Si p-type substrate. A post-growth exposure to hydrogen plasma resulted in active photovoltaic device with V_{OC} up to 480 mV. This indicates that hydrogen is able to passivate interface states at the p-n junction at the depth of as much as 10 μm which is deeper than normally observed. This may be attributed to grain boundary diffusion in the polycrystalline film. Our results strongly suggest that useable solar cell may be prepared from such inexpensive and low quality material as MG silicon.

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