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Effect of hydrogen passivation on polycrystalline silicon thin films

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Abstract

Hydrogen passivation is essential for improving the properties of polycrystalline silicon thin films. We have observed that remote plasma hydrogenation with duration up to 30 min effectively passivated the defects and improved the Hall mobility, trap density and photoluminescence intensity. Over 60 min of hydrogenation caused the photoluminescence intensity to decrease. It seems that excessive hydrogenation not only passivated defects but also created new defects (Si–H_2 bonds and hydrogen molecules) in the grains. Raman spectroscopy detected that hydrogen formed Si–H_2 bonds in the poly-Si up to 100 nm from surface. Creation of these defects corresponded to a decrease of the photoluminescence intensity. These defects might be harmful to poly-Si-based devices.

Keywords: Hydrogen passivation; Polycrystalline silicon; Photoluminescence; Raman spectroscopy; Si–H_2 bonding; Hydrogen molecules

1. Introduction

Polycrystalline silicon (poly-Si) is a material widely used in the semiconductor industry. It is particularly interesting, for example, for the photovoltaic industry as an attractive base material for solar cell applications. Performance of polycrystalline silicon thin film solar cells largely depends on transport properties dominated by grain boundaries. Hydrogen passivation can reduce the grain boundary defects and it is considered essential for improving the solar cell efficiency.

2. Experimental

Thin film poly-Si grown by atmospheric pressure chemical vapour deposition (APCVD) was deposited with SiH_2Cl_2 and BCl_3 as source and doping gases, respectively, directly on SiO_2 film fabricated by wet oxidation process of P^+ c-Si wafer with low resistivity ~0.002 Ωcm. Holes with 80-μm diameter were opened by photolithography in the SiO_2 at interval of 450 μm in order to contact the backside electrode for getting map of local currents measurement. In order to obtain poly-Si films with high crystallinity and large grain size, we deposited poly-Si films using the two-step method [1]. Polycrystalline silicon fabricated by this method has a columnar structure with (220) orientation and average grain size of 2 μm on average. The thickness of the poly-Si layer was 12 μm.

Hydrogen passivation of poly-Si thin films was performed with the remote plasma system in order to prevent surface damage by ions. The flowing gas was a mixture of H_2: 5 sccm and Ar: 0.3 sccm, the pressure was set to 1.0×10^{-2} Pa, the substrate temperature to 300 °C and the RF-power to 200 W. Hydrogen passivation time varied from 5 min to 60 min. In order to investigate the hydrogen passivation effect atomic force microscopy (AFM) combined with the mapping of local conductivity was chosen [2]. The combined AFM system was located inside the UHV chamber (10^{-8} Pa) to prevent the oxidation of surface. The van der Pauw technique was used to measure the Hall effect and its temperature dependence. Photoluminescence measurements at 7 K were performed on sample immersed in liquid He. PL spectra were analysed with the Ge detector

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and lock in amplifier. PL was excited by the Ar laser with the wavelength of 488 nm and the power density on the sample 5 mW/cm^2. Raman spectroscopy was used to observe local vibration modes (LVM) of Si–H$_2$ bonds in a stretching mode near the 2100 cm^{-1} line and hydrogen molecular (H$_2$) vibrations near the 4160 cm^{-1} lines. The Raman scattering spectra were taken in the backscattering geometry using excitation by the Ar laser at 514 nm.

3. Results and discussion

3.1. Map of local currents

Fig. 1 shows the map of local currents of both as-deposited poly-Si and hydrogenated poly-Si (60 min). The as-deposited poly-Si showed contrasted map of local currents due to different conductivities of various grains isolated by grain boundaries.

On the other hand, the map of local currents of hydrogenated poly-Si did not show the contrast comparable to that of as-deposited poly-Si. This finding agrees with another observation of the same behaviour by different method [3]. To our knowledge, this is the first time the changes in local currents due to hydrogen passivation are reported.

3.2. Hall mobility

Results of the carrier mobility, its activation energy and the trap state density measured and estimated by Hall effect are shown in Fig. 2 [4]. It can be seen that after only 5-min hydrogen passivation, the electronic properties of poly-Si were dramatically improved compared to that of as-deposited poly-Si. Improvement of poly-Si properties was saturated for hydrogenation times over 30 min. Hydrogen effectively passivated the defects at grain boundaries and suppressed the band bending at grain boundaries, which act as barriers for majority carriers and recombination sites for minority carriers. Properties of our poly-Si were dominated by grain boundaries and the decrease of the trap density at grain boundaries by hydrogenation led to the suppression of the band bending and the improvement of carrier mobility.

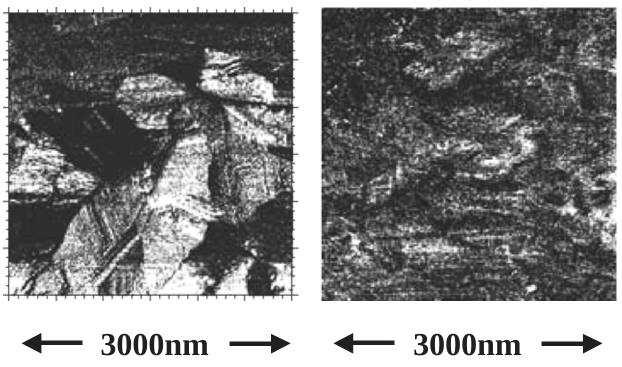

Fig. 1. Map of local currents measured by AFM with conductive cantilever on as-deposited (left) and on hydrogenated (right) poly-Si samples.

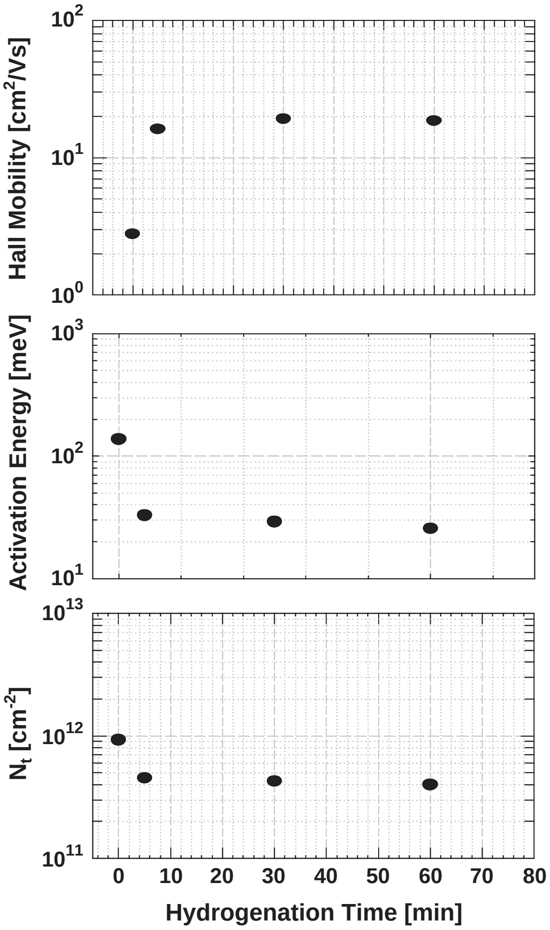

Fig. 2. Effect of hydrogenation on electronic properties of poly-Si observed by Hall measurements.

However, many researchers reported that hydrogenation could influence Si in two ways: passivates the defects by hydrogen bonding and also generates new defects [5]. Such a surface damage region must be very thin compared to the thickness of our poly-Si thin films (12 μm) because it cannot be seen by Hall measurement that averages over the whole poly-Si thickness.

3.3. Photoluminescence

Photoluminescence spectra (see Fig. 3) revealed a peak around 0.98 eV attributed to band tail-to-tail luminescence [6]. No sharp excitonic transition around 1.1 eV as in c-Si was observed.

The grain boundaries give rise to localized states in the band gap such as Si dangling bonds and strained Si–Si bonds, the latter of which are widely believed to be the origin of exponential band tails [3]. PL spectra of poly-Si show a broad peak at an energy somewhat smaller than the energy of the optical gap. In LPCVD grown poly-Si the