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Impurities and defects in multicrystalline silicon for solar cells: low-temperature photoluminescence investigations

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Abstract

The low-temperature photoluminescence (PL) measurements (down to 4.2 K) were employed for the investigations of the defects and impurities in multicrystalline silicon (mc-Si) samples grown by block-casting method. The optical properties of as-grown, irradiated by gamma-rays, heat and hydrogen plasma treated samples were studied. It was found that carbon and oxygen as the residual impurity atoms are responsible for the formation of the zero-phonon PL lines with 0.9355 eV (T line) and 0.9652 eV (I line) after heat treatments at about 350–550°C. The appearance of PL lines with the energies of 0.9697 eV (A line) and 0.7894 eV (C line) after a gamma-rays irradiation can be attributed to the formation of carbon- and oxygen-related centers, respectively. The comparison of the PL properties of the mc-Si samples with the mono-crystalline one is performed. It is shown that the main peculiarities of the low-temperature PL spectra of mc-Si can be explained both by the influence of residual impurities and the residual strains in this material.

Keywords: mc-Silicon; Photoluminescence; Strains; Residual impurity atoms

1. Introduction

Multicrystalline silicon (mc-Si) has been provided to be a material with exceptional promising for practical use as a base layer in solar cells. The maximum

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conversion efficiencies achieved experimentally are still not higher than about 18% in spite of numerous attempts to improve the cell performance and the preparation techniques. The recombination activity of impurities and intrinsic defects of the material, which is far from being understood, is one of the main limiting factors for mc-Si solar cells efficiencies [1,2]. In mc-Si these defects can be also formed both in the bulk and at the grain boundaries in mc-Si. It is evident that some of these defects can act as undesirable recombination centers reducing the energy conversion efficiency [1–3]. Therefore a further improvement of the efficiencies for multi-Si photovoltaic devices can be achieved by the reduction of the concentration of these defects or their passivation that needs a more deep understanding.

The objective of the work is the investigations and characterization of low-temperature (down to 4.2 K) photoluminescence (PL) of mc-Si. The goal is to identify the role of the various intrinsic defects in as-grown mc-Si as well as those resulting from high-energy particle irradiation, hydrogen plasma and thermal treatments, and to compare the PL spectra in mc- and mono-Si samples Czochralski (Cz) and float zone (FZ) grown.

2. Experimental

The material employed in this work was boron-doped mc-Si (Baysix mc-Si) from Bayer Solar GmbH, grown using block-casting technique. For scanning PL study at the temperatures of 4.2, 78 and 300 K the samples were cut to the dimensions of $1 \times 1\,\mathrm{cm}^2$. FZ Si samples doped with boron ($\sim 10^{16}\,\mathrm{cm}^{-3}$) were used as references. Some samples were irradiated by ^{60}Co gamma-rays with a flux of $5 \times 10^{16}\,\mathrm{cm}^{-2}$. The samples were then annealed at 200°C and 400°C in vacuum for 20 min. Thermally induced defects were formed in wafers subjected to a isothermal annealing at 450°C for 22 h. In some cases the hydrogenation was done at 260°C for 1 h (HF plasma 110 MHz, 50 W power, 400 mTorr pressure, 200 sccm hydrogen flux). For PL measurements the samples were immersed in liquid nitrogen or helium. The PL excitation was done by the 514.5 nm (or 488 nm) line of an Ar ion laser with power typically 50–150 mW. The diameter of the laser spot on the sample surface was varied from 0.1 to 4 mm using special focusing of optical system. Scanning PL measurements were performed with focused laser beam ($\sim$0.1 mm) and controlled X–Y moving of the sample immersed in liquid-nitrogen or helium. The light emission from the sample was analyzed by MDR23U spectrometer with 600 grooves/mm and detected with a liquid-nitrogen-cooled germanium p–i–n detector. The detector output was controlled by usual lock-in techniques.

3. Results and discussions

Fig. 1a shows the PL spectra of the as-grown Baysix mc-Si measured at three different temperatures. The PL spectrum at 4.2 K consists of two characteristic spectral regions. The first one, in the high-energy near-band-edge region, shows the

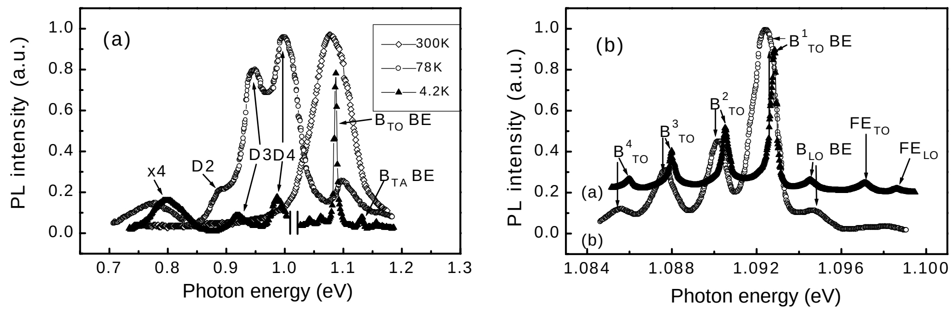

Fig. 1. (a) PL spectra of mc-Si at 4.2, 78 and 300 K with spectral resolution of 1, 2 and 3 meV, respectively; (b) The TO phonon-assisted PL lines of the bound excitons (BE) in B-doped FZ Si (a) and mc-Si (b). Spectral resolution ~0.2 meV (4.2 K).

transverse optical (TO) phonon replica at 1.0924 eV of the bound excitons (BE) at boron atoms. The second one, in the region below about 1.02 eV, includes additional low-intense spectral bands at 0.80, 0.904, 0.946 and 0.998 eV. More clear these peaks are seen in PL spectrum at 78 K. The spectral position of the low-energy peaks are the same at 4.2 K. The free exciton PL band at 1.10 eV is also observed in the high-energy region of the spectrum. The strongest features at 78 K are the dislocation-related bands at 0.904, 0.946 and 0.998 eV which are labeled as D2, D3 and D4, respectively [4–7]. At room temperature the PL spectrum contains only the broad peak at 1.08 eV which belongs to the phonon-assisted band-to-band emission. In addition to the results reported in Refs. [2,3], we found that the PL intensity of the D2–D4 dislocation-related lines and the defect-induced wide band 0.80 eV are more intensive (about of 5–10 times) for the near boundary regions when the excitation laser spot was scanned over the sample surface at low-temperatures (4.2 and 78 K). The energy position of the main D2–D4 lines and 0.8 eV band was varied in the range of ± 5 and ± 20 meV, respectively, under scanning the focused laser beam along or across the grain boundaries. This experimental fact shows the inhomogeneous distribution of the dislocations and defects in mc-Si. It is necessary to note that the 0.8 eV band has been recently observed in PL spectra of Si crystals implanted with H^+ and O^+ ions after the high-pressure–high-temperature treatments [8]. This band was also detected after the H^+ or He^+ ion implantation and subsequent high-temperature annealing at 1000°C [9]. One of the possible explanation is that the 0.8 eV band is related to the dislocation D1 line which has the spectral position at 0.81 eV [4–7]. From the other side, the slightly different spectral shape and energy position (of about 0.76–0.80 eV) allow to assume that the gettering of residual impurities such as carbon and oxygen as well as the self-interstitials during the growth of mc-Si can be responsible for the appearance of this band. Fig. 1b shows the PL TO phonon-assisted spectra of mc-Si (b) and FZ Si (a) samples. The TO and LO phonon-assisted free-exciton (FE) lines intensity FE (TO) and FE (LO) are relatively weak. The full width at half maximum (FWHM) of main bound exciton (BE) B_{TO} lines in Si crystals was found to be about of 0.4 meV at 4.2 K (curve (a) in Fig. 1b). This value is in a good agreement with data reported earlier [10]. One can see from curve (b) in Fig. 1b that the B_{TO} (BE) lines in mc-Si (near grain boundaries) are slightly shifted to lower-energy side. The FWHM of these lines at 4.2 K is about of 1.2 meV that is in 3 times higher than for FZ Si samples. The shifts and broadening of the B_{TO} (BE) lines are due to the residual strains which appears from the inhomogeneous distribution of dislocations and point defects near grain boundaries of mc-Si samples. Using the deformation potential constants measured by Balslev for Si [11] and data on the influence of the uniaxial strains on the PL spectra of B-doped Si [12] we estimated the value of the residual strains from the B_{TO} (BE) line shift and its FWHM as 5–15 MPa in the near grain boundary regions of mc-Si. It is well known that thermal treatments of Cz or FZ Si at 350–550°C lead to the optical activation of the defects which incorporate the oxygen and/or carbon atoms [13–15]. This method of the residual impurities optical activation has been used in our investigations for mc-Si samples subjected to thermal treatments.

Fig. 2 shows the PL spectra for both as-grown and as-grown and hydrogenated samples after the following annealing at 450°C for 22 h. One can see that two low-intensive zero-phonon lines T (at ~0.9355 eV) and I (at ~0.9652 eV) appear in PL spectra. One can see also that the relative intensity of the T and I lines are more high (about of 10 times) if the hydrogen plasma treatment was applied before the annealing. This might be an additional confirmation of the hydrogen atom incorporation in the structure of the T and I lines-related centers. It was shown [13,16,17] that the PL centers responsible for the appearance of the T line are created in either FZ (Cz) grown silicon by irradiation (electrons, neutrons) and subsequent thermal treatment in the temperature range of 400–600°C, or by thermal treatment in carbon-rich Cz Si. Recently, it has been shown that the T center contains two nonequivalent carbon atoms and one hydrogen atom [18]. The detection of the T line after thermal treatment of our mc-Si strongly confirms the presence of carbon and hydrogen atoms as unintentional impurities in as-grown material. It was also found that the I center has the same C–C–H core as the T center which includes in addition the oxygen atoms [18]. Therefore, the appearance of the T line gives the evidence that

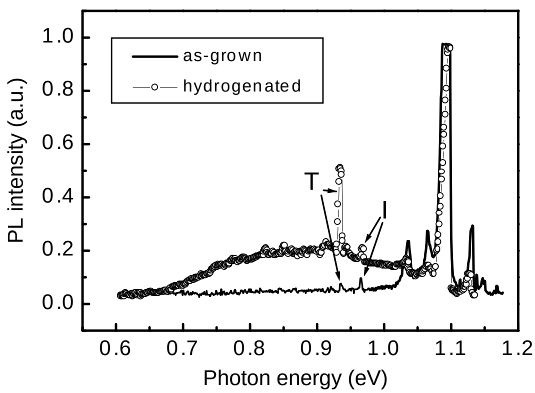

Fig. 2. PL spectra of as-grown (cut and chemically etched) and as-grown + hydrogenated mc-Si with following annealing at 450°C for 22 h.

oxygen atoms are also responsible for the defect complex formation in mc-Si at thermal treatments.

It is well known that irradiation of Cz and FZ Si by high-energy particles is the effective method to activate the residual impurities [19–21]. We studied the formation of the impurity-defect complexes in mc-Si after the gamma-ray irradiation with the dose of $5 \times 10^{16}\,\mathrm{cm}^{-2}$. Fig. 3 shows the PL spectra obtained from mc-Si after the irradiation and following annealing. The lines, labeled as A, C, T, I, H, are attributed to the zero-phonon transitions for different impurity-related defects. The PL spectrum observed before annealing includes two electron-vibronic bands: C (0.7894 eV), A (0.9679 eV) and FE and boron bound-exciton lines. Annealing of irradiated mc-Si wafers at 200°C results in decrease and relative redistribution of the intensity of C and A bands. Annealing at 400°C produces additional zero-phonon lines: H (0.9259 eV), T (0.9355 eV), I (0.9652 eV). The nature of the centers associated with A, C, T, I, H PL lines is well defined for silicon crystals and includes above mentioned (oxygen, carbon, hydrogen) impurities [19–21]. Fig. 4 shows the high-resolution fine structure of the A (0.9697 eV) line at 4.2 K for FZ-Si and mc-Si samples.

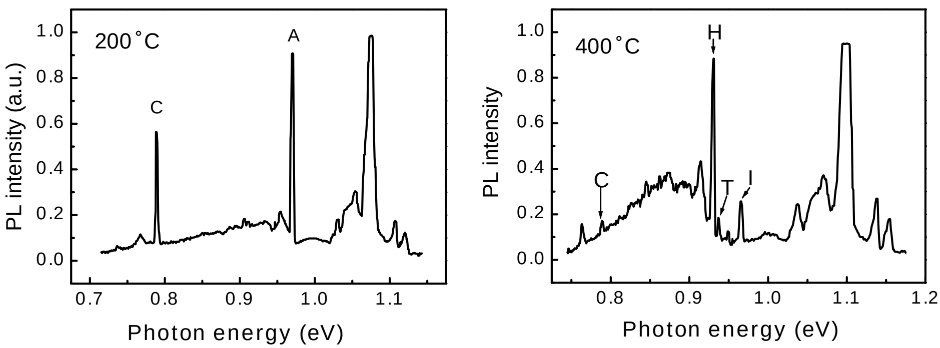

Fig. 3. PL spectra of mc-Si irradiated by ^{60}Co gamma-rays and annealed at 200°C and 400°C for 20 min.

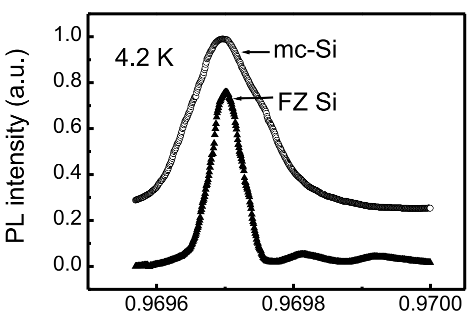

Fig. 4. Fine structure of the A line PL spectra of mc-Si and FZ Si samples at 4.2 K. Spectral resolution is 0.05 meV.

One can see that the line in high-quality FZ Si crystals has a triplet structure due to three silicon isotopes (Si^{28}, Si^{29}, Si^{30}) with the natural relations of 0.922:0.047:0.0031, respectively. Two carbon atoms C_i and C_s also involved in the structure of the A center [20]. For mc-Si wafers we were not able to resolve this triplet structure because of the internal stresses in this material. The FWHM of the A line in mc-Si material was measured to be $\sim$0.15 meV. Using this value and well-known piezo-optical parameters from uniaxial stress splitting of the A line [19] we estimated the value of the strains as $\sim$10 MPa.

4. Conclusions

Our experimental results can be summarized as follows:

- The impurities due to unintentional technological contaminations (hydrogen, carbon, oxygen) determine the structure of main point-like defects in mc-Si.
- PL spectra of such optically active defects show peculiarities (broadening and shifting of the PL lines) because of internal strains in mc-Si.
- Atomic hydrogen can accelerate the complex formation processes in mc-Si at 450°C annealing.
- The strain strength in mc-Si wafers is evaluated to about 10 Mpa.

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