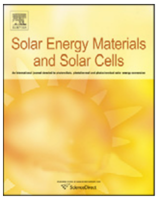
Solar Energy Materials & Solar Cells 94 (2010) 1907–1911

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat



Thermal stability of intermediate band behavior in Ti implanted Si

J. Olea*, D. Pastor, I. Mártil, G. González-Díaz

Dpto. De Física Aplicada III (Electricidad y Electrónica), Facultad de Ciencias Físicas, Universidad Complutense de Madrid, E-28040 Madrid, Spain

ARTICLE INFO

Available online 29 July 2010

Keywords:
Titanium
Silicon
Intermediate band
Ion implantation
Pulsed laser melting

ABSTRACT

Ti implantation in Si with very high doses has been performed. Subsequent Pulsed Laser Melting (PLM) annealing produces good crystalline lattice with electrical transport properties that are well explained by the Intermediate Band (IB) theory. Thermal stability of this new material is analyzed by means of isochronal annealing in thermodynamic equilibrium conditions at increasing temperature. A progressive deactivation of the IB behavior is shown during thermal annealing, and structural and electrical measurements are reported in order to find out the origin of this result.

1. Introduction

Since the increasing of efficiency of solar cells by intermediate band (IB) transitions was first formulated [1] on the basis of a previous work [2], intensive theoretical and experimental efforts have been conducted in order to produce IB materials [3–8]. It has been argued [9] that any semiconductor in which deep level impurities are introduced may have IB behavior if the concentration of these impurities is enough to overcome the Anderson–Mott transition limit [10,11], taking place an overlapping of the electron wavefunctions and giving rise to a new band inside the host semiconductor bandgap. This overlapping process would be a smooth transition, rather than have a step limit, and an IB would be formed gradually as impurity concentration is increased. A model that describes a situation where all impurities are equispaced yields a critical impurity concentration of $N_T = 5.9\times10^{19}\ \mathrm{cm}^{-3}$, concluding that above this concentration the electrons are delocalized [9].

Recently, we have studied the IB formation in Si with Ti as deep level [12]. We have measured the electrical properties of this promising material, which are an example of a typical impurity band conduction behavior [13,14]. Moreover, a slight but remarkable increase in the minority carrier lifetime with Ti concentration has been measured [15], which could be one indication of IB formation. Later, it has been suggested by means of theoretical calculations that interstitial Ti at high concentration would form a partially filled IB in Si, while substitutional ones would form an empty IB [16]. Rutherford backscattering measurements showed that annealing of Ti implanted Si by means of pulsed laser melting (PLM) would place Ti mostly in interstitial sites [12], supporting these results.

PLM annealing with excimer lasers such as KrF and XeCl is becoming one of the most promising method to produce IB thin layer materials given that it is a very powerful technique for recovering the crystal lattice after ion implantation processes, added to the very low diffusion of the implanted impurities due to the short recrystallization times (10^{-8}–10^{-6} s) [17,18]. Highly non-equilibrium techniques such as ion implantation and PLM annealing are necessary to achieve the high concentration needed to reach the Mott limit, usually over solid solubility limit; thus structural studies of PLM effects on bulk semiconductors are of great interest [19,20].

The anomalous behavior in the electronic transport properties of PLM annealed high dose Ti implanted Si that is well explained with an IB conduction has been described elsewhere [13]. A decoupling effect between the implanted layer and the substrate takes place for temperatures below 200 K and it seems to be associated with IB formation. The decoupling has been attributed to a rectification phenomenon due to the low carrier concentration in the conduction band of the implanted layer that avoids conduction through the implanted layer to the substrate at low temperatures. Carrier concentration in the conduction band of the implanted layer is modeled with a temperature-dependent thermal activation from the IB level. It is suggested that at very low temperature conduction takes place mostly in the formed impurity band, which exists only in the implanted region, and therefore has no continuity to the substrate. In this way, at low temperatures conduction is restricted only to the surface layer. The impurity band acts as a degenerate band, with a very high carrier concentration and a very low mobility. Therefore, IB properties can be measured at very low temperature, where the substrate is fully decoupled. At temperatures close to 300 K, where thermal activation leads to a great increase in the carrier concentration in the conduction band of the implanted layer, the rectification effect is not presented, and the electronic transport properties can be analyzed assuming that the implanted layer and the substrate are two independent paths of conduction in parallel.

---

* Corresponding author. Tel.: +34 913 94 44 34; fax: +34 913 94 51 96.
E-mail address: oleaariza@fis.ucm.es (J. Olea).

0927-0248/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2010.06.045

Since the substrate has a thickness several orders of magnitude higher than the thickness of the implanted layer, conduction at room temperature is carried out mainly by the substrate, although conduction through the implanted layer, partly by the conduction band and partly by the IB, is not negligible. In this analysis the valence band is not taken into account since the carrier concentration in this band is not significant.

Apart from annealing techniques to obtain good quality crystalline materials after ion implantation, studies regarding later thermal treatments are mandatory since any material has to tolerate a certain thermal budget during the subsequent processes necessary to produce the final device. The aim of this paper is to analyze the thermal stability of the IB-like behavior recently discovered in high dose Ti implanted Si samples by isochronal annealings after PLM treatments. Structural and electrical measurements are performed in order to find out the effects of annealing in thermodynamic equilibrium conditions in this new material.

2. Experimental

Single crystal (1 1 1) n-Si 300 μm thick $1\times1\,\text{cm}^{-2}$ square samples with a resistivity $\rho=200\,\Omega\,\text{cm}$, a mobility $\mu=1250\,\text{cm}^2/\text{V s}$ and a carrier concentration $n=2.2\times10^{13}\,\text{cm}^{-3}$, measured at 300 K were implanted with Ti ions at energies in the range 20–35 keV by means of a VARIAN CF3000 Ion Implanter refurbished by IBS, with doses in the range 10^{15}–$10^{16}\,\text{cm}^{-2}$. Subsequent annealing by the PLM method with one 20 ns long pulse of a KrF excimer laser (248 nm) at an energy density of $0.8\,\text{J/cm}^2$ was carried out to recover the crystallinity of the implanted layer [12]. PLM annealing processes were performed by J.P. Sercel Associates Inc. (New Hampshire, USA). Al contacts of 200 nm of thickness were evaporated in the corners by means of the e-beam method. After evaporation, some of the samples were thermal annealed by 5 min isochronal processes at increasing temperatures from 200 to 500 °C. Electrical characterization for each isochronal annealed sample was made without removing the initial Al contacts. As the Ti concentration is extremely high, it should act as a good diffusion barrier up to 500 °C, avoiding a short-circuit formation between the contact and the substrate [21].

Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) characterizations were carried out with a TOF_SIMS IV model manufactured by ION-TOF, using a 25 keV pulsed Bi^{3+} beam at 45° incidence. The secondary ions generated were extracted with a 10 keV voltage and their time of flight from the sample to the detector was measured in a reflection mass spectrometer. Calibration was conducted obtaining Ti signal in relation to a non-saturated reference ion (Si^{28}) in order to correct the secondary ion yield, roughness and instrumental effects. Final calibration was realized using reference unannealed samples implanted at 32 and 33 keV with 10^{15} and $2\times10^{16}\,\text{cm}^{-2}$, respectively.

Sheet resistance and Hall effect at variable temperature were measured with a Keithley SCS 4200 model from 90 to 380 K by means of the van der Pauw set-up, placing the samples in a homemade cryostat attached to a vacuum pump to avoid moisture condensation. A Kepco BOP 50–20 MG bipolar power supply was used to fed the electromagnet and changing the magnetic flux direction in the four rotated equivalent configurations of the van der Pauw technique we minimized the thermo-galvanomagnetic effects.

3. Results and discussion

Low implantation energy is always needed in order to obtain a superficial layer, since PLM with this kind of excimer lasers usually melts in the range of several tens of nanometers with the conditions summarized before [22]. The minimum PLM energy density needed to melt the implanted layer is between 0.4 and $0.6\,\text{J/cm}^2$, although the optimum energy density is about $0.8\,\text{J/cm}^2$. This optimum energy density produces a low defective IB layer, depending also on the implantation dose, which translates in high mobility [23]. The mobility of the sample implanted with $10^{15}\,\text{cm}^{-2}$ and annealed at $0.8\,\text{J/cm}^2$ is almost equal to the mobility of the substrate at room temperature. As implantation dose increases, the effective carrier concentration also increases and the effective mobility is reduced. Increasing the PLM energy density over $0.8\,\text{J/cm}^2$ will eventually set the annealing in a thermodynamic equilibrium regime since the thicker the melted layer, the longer it lasts to recrystallize and the advantage of the technique would be lost [24,25]. Moreover, a certain quantity of Ti is always expelled in the PLM process and this quantity increases with the energy density of annealing. Therefore, to increase the probability of having IB behavior, with lower doses higher implantation energy was used.

The stability of the IB behavior was studied by means of isochronal annealings on Ti implanted Si and subsequently PLM annealed samples. ToF-SIMS measurements of a sample implanted with $10^{15}\,\text{cm}^{-2}$ at 32 keV and PLM annealed at $0.8\,\text{J/cm}^2$, and of an equivalent sample after 5 min isochronal annealings from 200 to 500 °C are presented in Fig. 1. The as-implanted reference sample is also shown. In the profiles of the samples PLM annealed, the valley at about 40 nm could be related with the depth of the melted region [26]. Ti atoms below this point have been pushed to the surface of the sample during liquid phase recrystallization [17] and are the main origin of the IB behavior [13]. Ti atoms in the non-melted region have been probably only heated and annealed close to a thermodynamic equilibrium regime. Ti concentration in this region is below the theoretical Mott limit. These results show that the post-PLM annealing processes did not produce a great effect in the ToF-SIMS profile, and only a little difference is observed in the surface peak. It is known that Ti has a very low diffusion coefficient [27], and it is shown to be true even with the extremely high concentration measured. Moreover, diffusion of impurities is usually much higher in an amorphous host semiconductor than in a crystalline ordered one; therefore isochronal annealings up to 500 °C did not produce a noticeable Ti diffusion since the lattice

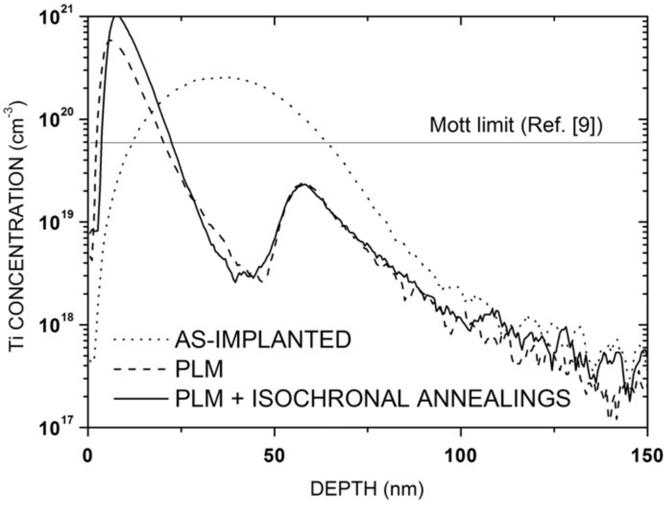


Fig. 1. ToF-SIMS measurements of a sample implanted with $10^{15}\,\text{cm}^{-2}$ at 32 keV and subsequently PLM annealed with $0.8\,\text{J/cm}^2$ and of the same sample after 5 min isochronal annealings at 200, 300, 400 and 500 °C. A non-annealed reference sample implanted with $10^{15}\,\text{cm}^{-2}$ at 32 keV and the theoretical Mott limit are also shown.