Thermal stability of defects introduced by electron beam deposition in p-type silicon

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ABSTRACT

The electronic and thermal properties of defects introduced during electron beam deposition (EBD) followed by isochronal annealing of titanium (Ti) contacts on p-Si were investigated. In this work, EBD-deposited Ti Schottky contacts were annealed within a temperature range of 200–400 °C. Current-voltage (*I-V*) measurements were conducted to monitor the change in electrical characteristics with every annealing step. A barrier height of 0.55 eV was measured on the as-deposited sample. Deep level transient spectroscopy (DLTS) and Laplace-DLTS techniques were employed to identify the defects introduced after EBD and isochronal annealing of the Ti Schottky contacts. DLTS revealed that the main defects introduced during metallization were hole traps H(0.05), H(0.23) and H(0.38). Annealing at 300 °C removed the two hole traps H(0.05) and (0.38). Atomic force microscopy (AFM) was performed on the contacts to monitor their surface topology. The surface of the contacts became rougher as the annealing temperature increased. The slight increase in root-mean-square roughness of the contacts with increasing annealing temperature may be attributed to outdiffusion of Si into Ti layers.

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1. Introduction

Metallization is a fundamental practice in silicon technology. Electron beam deposition (EBD) of metals is often used due to its ability to deposit high melting point metals and because this can be done at accurately controlled rates. It has, on the other hand, been shown that EBD of metals on semiconductors introduces electrically active defects at and beneath the semiconductor surface [1]. The origin of the defects was shown to be energetic particles accelerated from the vicinity of the electron filament onto the sample by the electric and magnetic fields present in the locality of the metal source [2]. These defects usually have an adverse effect on device performance, but may in some cases be beneficial [3].

The electrical properties of defects introduced in Si by EBD of metals have been previously reported. Some data is also available on the annealing of these defects, e.g. for Mo-Si contacts [1]. Annealing studies are usually hampered by the fact that Schottky contacts become too leaky for electrical measurements after annealing above 500 °C. However, a complete annealing study involving the removal of all defects, is vital in order to determine processing conditions for obtaining a defect-free space charge region below Schottky contacts formed by EBD.

In this study, we have investigated the thermal stability (in the range 200–400 °C) of Ti Schottky contacts and of the defects introduced in p-Si during electron beam deposition (EBD) of these contacts.

2. Experimental procedure

A p-type, boron-doped Si wafer with a carrier density of 3.4×10^{16} cm^{-3} was used for this study. Samples were prepared for metal deposition by cleaning them using a three step degrease in trichloroethylene, isopropanol and methanol for three minutes each in an ultrasonic bath. Hereafter, the samples were dipped in clean de-ionised water then in 40% HF for ten seconds and finally a rinse in de-ionised water. The samples were blow-dried with nitrogen and then immediately loaded into the vacuum chamber which was then evacuated to a pressure below 1×10^{-6} mbar to prevent oxidization before metallization.

Deposition of Ti was carried out using electron beam deposition (EBD). A mechanical mask was used for depositing well-defined circular dots of diameter 0.6 mm and a spacing of 1 mm between dots. A Varian 10 kW e-Gun in a high vacuum evaporation chamber was used for this process. The electron-gun has been designed with a 270° deflection angle for the electron beam and so that no contaminants from the heated tungsten filament can be deposited on the substrate. The crucible was water cooled to ensure safe

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operation even at full power. At the completion of the deposition process, the sample was removed from the vacuum chamber and prepared for *I-V* and *C-V* measurements.

Ti Schottky contacts with a thickness of 100 nm were deposited. These contacts were annealed in Ar at temperatures of up to 400 °C in 100 °C steps for 20 min periods. *I-V* and *C-V* measurements were used to monitor the quality of the Schottky contacts. Conventional and high-resolution Laplace-DLTS (L-DLTS) [4] was performed after each annealing cycle to monitor the presence of the EBD-induced defects and to obtain their electronic properties (activation enthalpy, E_T, and apparent capture cross section for carriers, σ_a). For comparison, a sample exposed to electron beams, a process known as electron beam exposure (EBE), was also characterised. During EBE, without metal deposition, the samples were exposed for 50 min; while the beam heated a tungsten source using a beam current of 100 mA, this current being insufficient to evaporate tungsten, thus exposing the samples to electron beam conditions comparable to those experienced during deposition [5]. Nickel (Ni) diodes were then fabricated on the sample using EBD. AFM analysis was performed on the as-deposited and annealed samples using the Bruker Dimension Icon Nanoscope 5 with ScanAsyst scanning probe microscope.

3. Results and discussion

3.1. Thermal stability of the Ti Schottky contacts

As-deposited metal-semiconductor contacts display non-ideal *I-V* characteristics. The experimental data were best fitted by the thermionic emission equation [6] which is given by

$$I = I_s \left[exp\left(\frac{qV}{nk_BT} \right) - 1 \right] \tag{1}$$

where I is the measured current, I_s is the saturation current, V is the applied voltage, q is the electronic charge, n the ideality factor, k_B is the Boltzmann constant and T is the absolute temperature. The saturation current, I_s is given by

$$I_s = A^* A T^2 \exp\left(-\frac{q\phi_B}{k_BT} \right) \tag{2}$$

I_s is determined from the extrapolated intercept of log I versus V curve on the y-axis.

Fig. 2. The DLTS spectra of the as-deposited sample, after annealing at 300 °C and at 400 °C measured at a rate window (RW) of 80 s^{-1}.

Fig. 3. The DLTS spectra of the EBD and EBE + EBD as-deposited samples measured at a rate window (RW) of 80 s^{-1}.

$$\phi_B = \left(\frac{k_BT}{q} \right) ln\left(\frac{A^* A^2}{I_s} \right) \tag{3}$$

where A^*, A and ϕ_B are the Richardson constant, the contact area and the Schottky barrier height respectively. Putting this value of
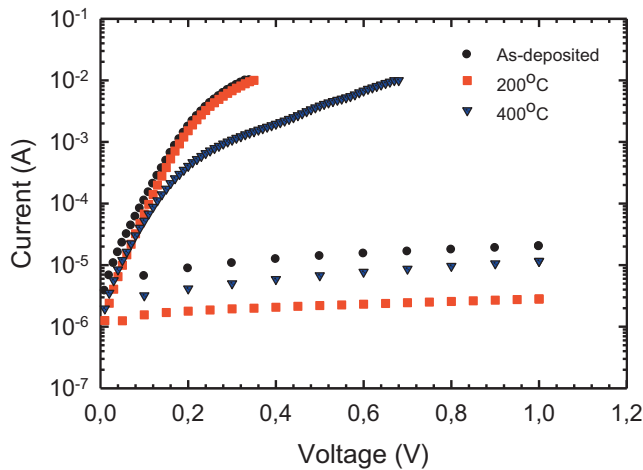

Fig. 1. The forward and reverse bias *I-V* characteristics of a Schottky contact after metallization (as-deposited), after isochronal thermal annealing for 20 min at a temperature of 200 °C and 400 °C, measured at room temperature.
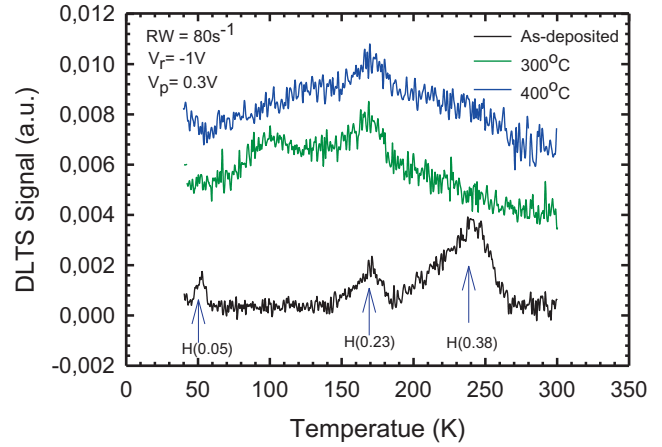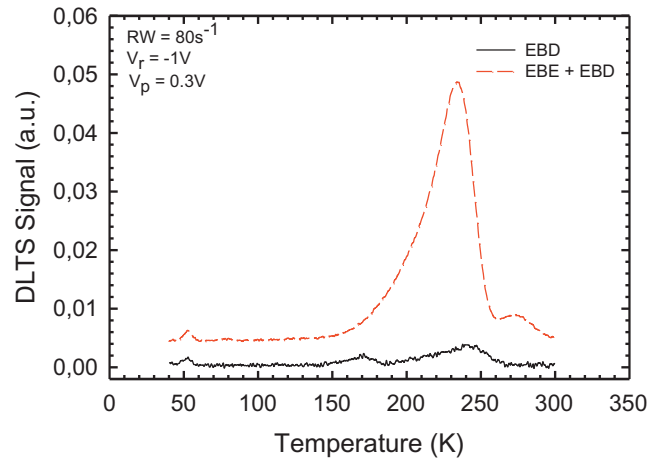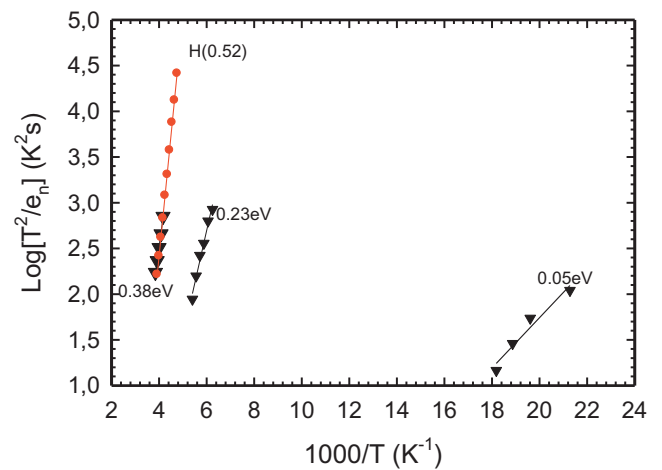

Fig. 4. The Arrhenius plot showing the defects present after: metallization (triangles) and electron beam exposure with electron beam deposition thereafter (circles).
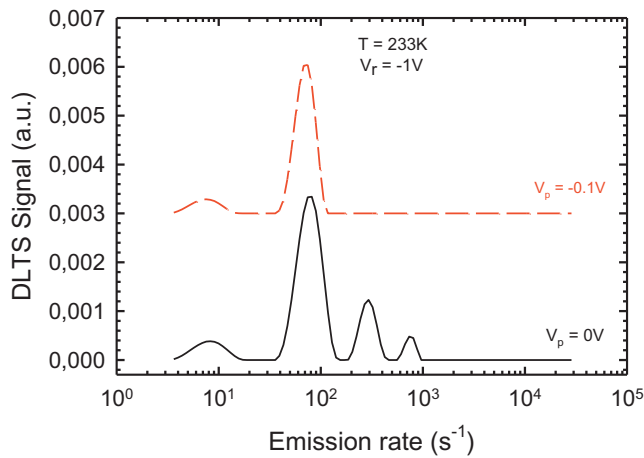
Fig. 5. The Laplace-DLTS spectrum clearly separating the signal of the EBE + EBD peak.

I_s in Eq. (3), the value of SBH is evaluated. From *I-V* measurements it was found that the barrier heights of Ti contacts directly after EBD were 0.55 eV. Fig. 1 shows that the Ti contact was affected by series resistance as the annealing temperature was increased. After annealing at 400 °C the Ti Schottky contacts degraded due to oxidation [7]. The barrier height of the Ti contact remained at 0.55 eV after annealing at 400 °C.

3.2. Electronic properties of EBD induced defects

DLTS revealed (Fig. 2) that the main defects introduced during metallization are H(0.05), H(0.23) and H(0.38). In this notation "H" means "hole trap" and the number after H is the activation enthalpy, in eV, obtained from an Arrhenius plot of log (T^2/e_n) vs 1000/T. Here e_n is the emission rate at temperature T. Annealing at 300 °C removed H(0.38) and H(0.05), while a new peak was introduced. The peak height was too small for resolution using L-DLTS as a result the peak's identity is not clear.

Two of the defects seen here are related to well-known radiation induced defects in Si. H(0.23) is the 0/+ charge state of the divacancy [8]. H(0.38) is introduced during electron irradiation, that was originally proposed by Mooney et al. to be associated with the carbon-oxygen-vacancy complex (V-O-C) also known as the K centre [8,9]. A defect at H(0.35) with a similar annealing behaviour has also been reported by Auret et al. after electron irradiation of p-Si, as well as after EBD of contacts on p-Si [1]. However, Trombetta et al. strongly demonstrated that this level is associated with the interstitial-substitutional carbon complex C_i-O_i [10]. The origin of H(0.05) is still the subject of speculation.

The conventional-DLTS spectra of the Ti contacts fabricated using EBD and the Ni contacts fabricated after EBE using EBD (EBE + EBD) are shown in Fig. 3. The EBE + EBD spectrum exhibits one prominent broad peak at 233 K and a small peak at 54 K which suggests that it is the EBD defect, H(0.05). In this study, the defects' electronic properties were extracted from the Arrhenius plots shown in Fig. 4. The activation energy calculated for the peak at 233 K was H(0.52).This defect may have been an EBD process induced defect. The defect's structure is still under investigation as are the rest of the peaks revealed by L-DLTS. Fig. 5 shows the high resolution L-DLTS spectra measured around the broad peak at −1 V reverse bias (V_r). L-DLTS separates the signals of the levels within that peak. The number of peaks was reduced by varying the filling pulse (V_p).

The aim of depth profiling was to find the defect concentration as a function of depth for individual defects. Fixed bias-variable pulse L-DLTS depth profiling [11,12] was used to measure the depth distribution of the defects investigated in this study. For each defect, the temperature was kept constant and the reverse bias of −2.5 V was maintained while varying the filling pulse. L-DLTS depth profiling showed that the concentration of all the defects reduced from the surface into the Si away from the junction. This was as a result of the fact that EBD introduces defects at and below the surface [1]. These defects have been shown to be produced by energetic particles accelerated from the locale of the electron filament onto the sample by the electric and magnetic fields present in the surrounding area of the metal source [2].

3.3. Morphology / surface topology of Ti contacts

AFM analysis revealed the topography of the samples used in this study. Fig. 6 displays images of Ti contacts obtained using
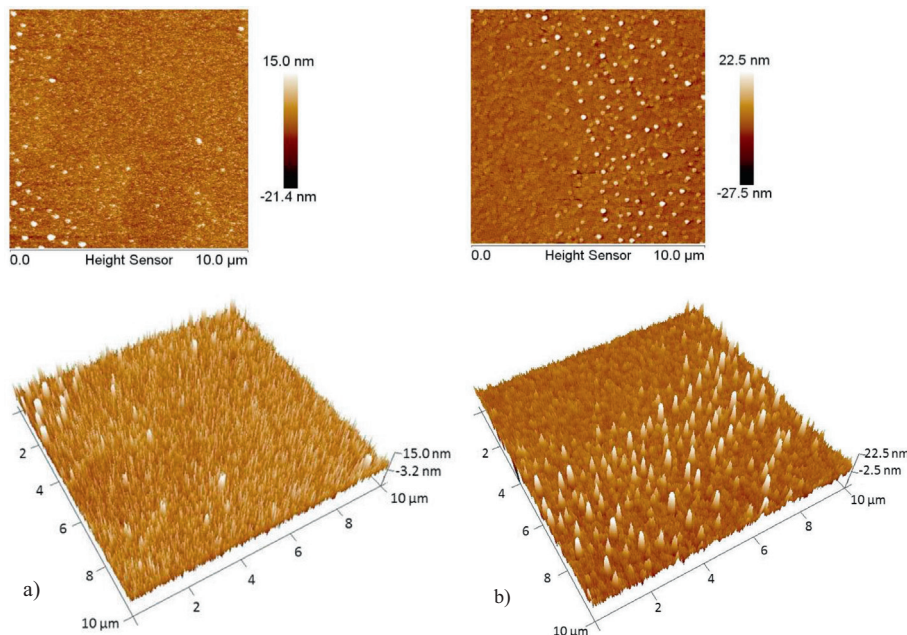

Fig. 6. 10 μm × 10 μm AFM 2-D and 3-D images of (a) the as-deposited sample and (b) after annealing at 400 °C.

ScanAsyst mode. The figure shows (a) the as-deposited sample and (b) the sample after annealing at 400 °C. The surface morphology of the as-deposited Ti/p-Si Schottky barrier diode is fairly rough with a root-mean-square (RMS) roughness of 3.43 nm. The roughness of the as-deposited SBDs may be attributed to damage from the electron beams during metal deposition [1]. The RMS roughness of the diodes increased with increase in annealing temperature. At annealing temperature of 400 °C, the surface morphology degraded slightly with RMS roughness of 4.15 nm. The degraded surface of the SBDs after the annealing may be as a result of outdiffusion of Si into Ti layers [13].

4. Conclusion

We have investigated the thermal stability (in the range 100–400 °C) of defects introduced in p-Si by EBD of Ti contacts as Schottky rectifiers. The Schottky barrier height remained at 0.55 eV after annealing at 400 °C. Series resistance affected the contacts as annealing temperature was increased. Three defects states were observed. H(0.23) and H(0.38) were states observed by other authors after irradiation H(0.23) was attributed to the divacancy of charge state 0/+. The level H(0.38) was associated with the K centre. The identity of H(0.05) is not yet known. AFM revealed that surface roughness increased with increase in annealing temperature. The origin of this surface roughening will be further investigated in future work.

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