# Thermal stability studies of platinum Schottky contacts on n- Si (111) and the defects introduced during fabrication and annealing processes.

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**Abstract.** The electron beam deposition process was used to fabricate Pt Schottky contacts onto n-Si (111). Subsequently these contacts were annealed at temperatures varying from 50°C to 600°C for ten minutes at each temperature. The forward *I-V* characteristics show that the diodes were stable at lower voltages and suffer series resistance effects at voltages higher than 0.5 V. The reverse *I-V* curves shows increasing leakage current with increasing annealing temperature. At lower annealing temperatures, the reverse leakage current is constant at about $10^{-9}$ A. The ideality factor increased from 1.02 to 2.61 while the barrier height decreased from 0.80 to 0.70 eV as the annealing temperature increased. DLTS revealed that electron beam deposition introduced defects which were identified as the E-centre (VP centre), the A-centre (VO centre), the interstitial carbon ($C_i$) and the interstitial carbon-substitutional carbon ($C_iC_s$) pair. Isochronal annealing at 10 minutes intervals revealed that the E-centre vanishes between 125 and 175°C annealing while the concentration of the A-centre increased in this range. The A-centre annealed out above 350°C and after 400°C, all the electron beam induced defects were all removed.

## 1. Introduction

Metal silicides have been used as electrical conductors in silicon integrated circuits (SIC) since the beginning of the $20^{th}$ century due to electrical properties such as low resistivities, easy fabrication and general stability in most processing techniques [1]. The resistivities of transition metal silicides are comparable with those of metals and metal-alloys, making this group of silicides good electrical conductors. Applications of metal-silicides have focused on Schottky barrier and ohmic contacts, gate and interconnection metal and as epitaxial conductor in heterostructures. Silicides with high melting points are attractive to use in high temperature device fabrication and operating environments [2]. In the fabrication of silicides, metals are deposited according to their melting points in different metallization systems. In particular, the electron-beam deposition (EBD) is used to deposit metals with high melting points, with an added advantage of uniform deposition rates. The EBD process, like many other metallization processes, introduces defects at and close to the metal-semiconductor interface, which has adverse effects on the device performance [3]. The defects responsible for the alteration of the barrier height of the metal contacts are those formed when energetic particles reach the semiconductor surface, creating damage in the lattice. In Si-based devices, defects created by proton and electron radiation increase the switching speed of the devices [4]. For high open circuit voltage Si photovoltaic devices, defect degradation in electrical properties of the device has been reported [5]. Defects introduced during EBD of metals on Si grown by Czochralski and float zone methods have previously been reported, where the E-centre (VP) and the A-centre (VO) appeared as dominant [6]. A defect similar to a divicancy was also observed [7]. The difference between the observed defects in reference [6] and [7] may be attributed to different EBD systems used, different vacuum conditions as well as the use of Si with different concentrations of impurities such as C and O In this work, Pt Schottky contacts on n-Si (111) were fabricated and electrical properties of the contacts were investigated. We also report on the electronic properties of defects introduced during metal deposition and the effects of annealing on the defects.

## 2. Experimental Procedure

We have used epitaxially grown, 12 μm thick, Si doped with P to a level of $3.5 \times 10^{15}$ cm$^{-3}$ grown on a n$^{++}$Si substrate for our investigation. Before metallization, samples were first degreased in trichloroethylene (TCE), isopropanol (ISO) and methanol for 5 minutes each followed by dipping into HF for 60 seconds. Immediately thereafter, the samples were loaded into the EBD vacuum system that was pumped down overnight to a pressure below $10^{-6}$ mbar. Pt Schottky contacts 0.6 mm in diameter and of various thicknesses were deposited in an EBD vacuum system through a mechanical mask. Typically, eight Schottky Pt contacts were fabricated onto piece of 3 mm x 5mm Si. A Varian 10 KW electron gun (model 989-1118) vacuum evaporation system was used for metallization of Pt. The vacuum before evaporation was $10^{-6}$ mbar and this would increase to $10^{-5}$ mbar during deposition. After contact formation, current-voltage (*I-V*) and capacitance-voltage(*C-V*) measurements were performed to assess the quality of the diodes and to determine the free carrier density of Si. It was found that the free carrier density of the EPI Si was $3.5 \times 10^{15}$ cm$^{-3}$. *I-V* and *C-V* measurements were repeated after every annealing cycle in Ar gas, for ten minutes from 50°C to 600°C in steps of 50°C. The diodes were irradiated with electrons from a Sr-90 source with a dose of up to $1 \times 10^{15}$ cm$^{-2}$.. Conventional DLTS was used to study defects introduced during the metallization and irradiation processes. High resolution Laplace DLTS was used to separate the conventional DLTS signals of defects with closely spaced energy levels. The signatures of the defects for electron traps, $E_\gamma$ and their apparent cross-section $\sigma_a$ were determined from Arrhenius plots of $\ln(T^2/e)$ versus $1000/T$, where $e$ is the electron emission rate and $T$ is the measurement temperature.

## 3. Results and Discussion

*I-V* characteristics of the diodes presented here are deduced from the thermionic emission current-transport model [1]. Figure 1 shows the semilog forward and reverse bias I-V characteristics of the samples in the annealing temperature range 100°C to 600°C. The forward I-V characteristics of the diodes annealed at temperatures up to 100°C show that the diodes were stable at lower voltages and suffer the series resistance effects at voltages higher than 0.5V. Series resistance increases sharply as the annealing temperature increases. Diodes annealed at temperatures higher than 250 °C suffer series resistance at voltages lower than 0.3 V. Figure 2 shows the graph of SBH and reverse leakage current at -1V as a function of annealing temperature. The reverse leakage current increased with increasing annealing temperature, from $9.4 \times 10^{-4}$ μA to $7.0 \times 10^{-2}$ μA. Throughout the annealing process the reverse leakage current at -1V remains in the same order of magnitude of μA. At about 300°C, the Schottky barrier height drops significantly while the reverse leakage current at -1V reaches its highest value.

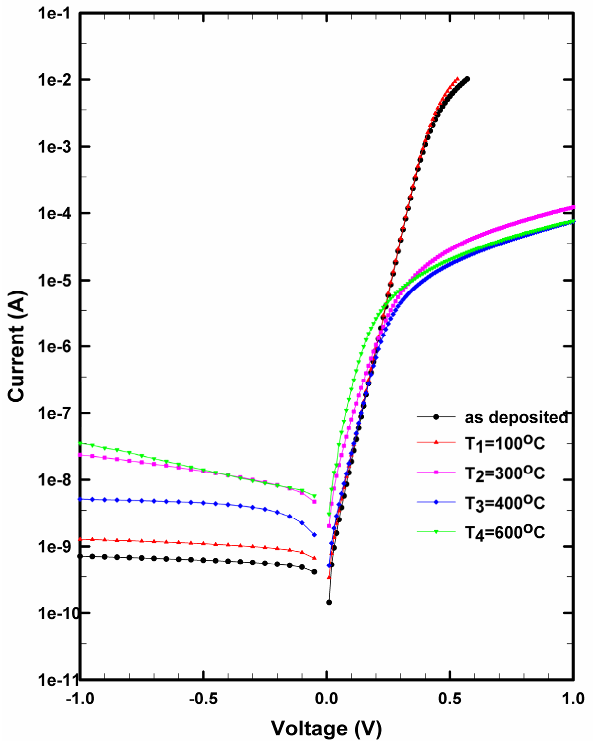



**Figure 1**: The I-V characteristics of SBD of Pt/n-Si(111) after isochronal thermal treatment at different annealing temperatures

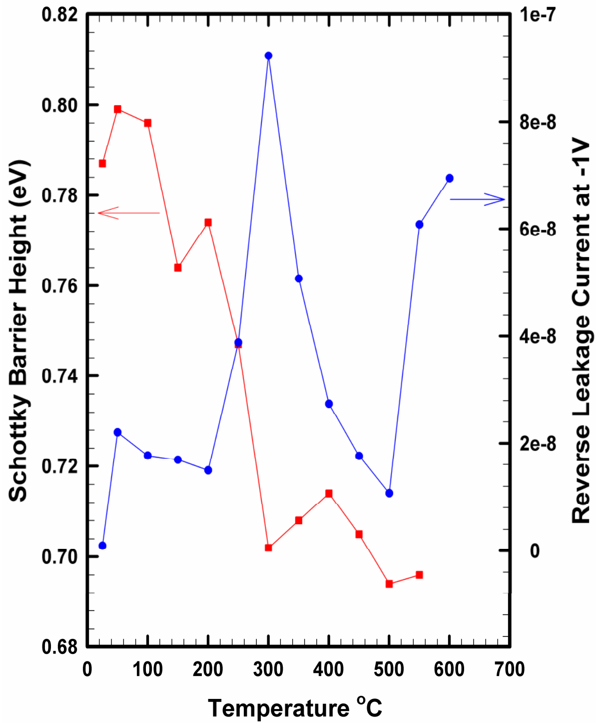
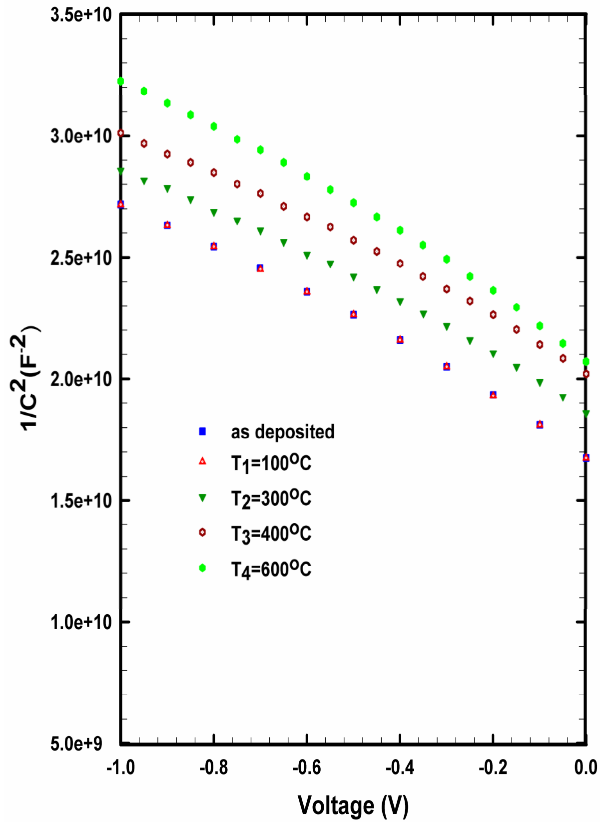



**Figure 2**: SBH and reverse leakage current at -1V factor as a function of temperature

Figure 3 shows the plots of Pt/n-Si Schottky barrier reverse biased $C^{-2}$-$V$ characteristics at 1.0 MHz for different annealing temperatures. The plots of $C^{-2}$ as a function of reverse bias voltage are near linear, indicating the formation of Schottky diode and constant non-compensated ionized donor concentration [8]. The SBH of the $C^{-2}$-$V$ plots were found to be 0.88 eV before annealing while the *I-V* barrier height was 0.80 eV. Due to different nature of measurements techniques, SBH obtained by *I-V* and *C-V* are not the same [1]. Figure 4 shows the SBH and the ideality factor as a function of annealing temperature. The Schottky barrier height (SBH) deduced from the thermionic emission current model, decreased from 0.80eV to 0.70 eV, while the corresponding ideality factor increased from 1.02 to 2.61 as the annealing temperature increased. At temperatures between 240°C and 260 °C there appears a clear transition for the diodes where the ideality factor, SBH and the reverse leakage current at -1V changes.



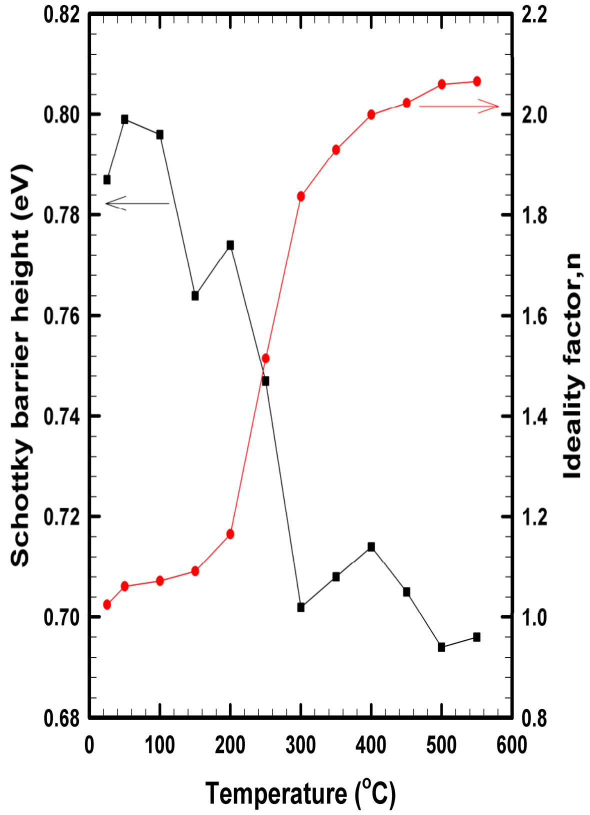




**Figure 3**: The C-V characteristics of SBD of Pt/n-Si(111) after isochronal thermal treatment at different annealing temperatures

**Figure 4**: SBH and ideality factor as a function of temperature

We suggest that there is significant reaction between Si and Pt to form a Pt-Si intermix (25°C to 200°C), $Pt_2Si$ (210°C to 280°C) and PtSi (280°C and 350°C). The changes in both SBH and ideality factor coincides with these three regions of Pt-silicidation: between 25°C to 200°C, 200°C to 300°C and 300°C and 550°C, as shown in Fig 4. It has been reported that Pt-Si starts forming at room temperature because of Pt atoms attaching themselves to Si atoms via the Si dangling bonds [10]. In addition, Larrieu et al has reported on the Pt-$Pt_2Si$-PtSi reaction chain completed within 2 minutes in the temperature range 300°C, 400°C and 500°C [11]. Furthermore, platinum silicides compounds are reported to grow sequentially as the temperature increases. $Pt_2Si$ phase grows between the 210°C and 280°C due to the diffusion of Pt atoms into bulk Si, a process that continues until all the Pt is depleted from the surface [10]. PtSi forms between 300°C and 350°C, starting from the interface between $Pt_2Si$ and Si, by in-diffusion of Si atoms into $Pt_2Si$ lattice. This process is very rapid and comes to completion in about 2 minutes at 350°C [12]. In this work, the diode characteristics show that there Pt on Si formed a rectifying metal contact where the diodes characteristics followed a known pattern where SBH decreases with increasing temperature and the ideality factor increases with increasing temperature. The SBH, ideality factor and reverse leakage current at temperatures between 240°C and 260°C shows that there is a transition of the metal contacts, where $Pt_2Si$ formed. The ideality factor is lowest at temperature range 50°C to 200°C and increases sharply from 200°C to 300°C, and then stabilizes after 300°C, further evidence due to different phase of silicide. The reserve leakage current is lowest at lower annealing temperatures, but increases immediately with increasing temperature. We have found that $Pt_2Si$ is a more stable compound for metal contacts for devices operating at lower temperatures while PtSi is suitable for devices operating at higher temperatures. In the case of solar cells which are exposed to radiation where temperatures fluctuate, a further study of PtSi as contact will be investigated.

Since we will be comparing the defects introduced during electron beam deposition (EBD) with those introduced by high energy (MeV) electrons, we first discuss the latter defects in n-type Si. High energy electron irradiation of Si introduces single vacancies and self interstitials that are mobile at room temperature [13]. These defects are created when the atoms are displaced by elastic scattering of the high-energy electrons. If a mobile interstitial moves next to a substitutional carbon ($C_s$) in the Si lattice, it may replace $C_s$ to create $C_i$, which is also mobile at room temperature [14]. The DLTS spectrum that we record after room temperature irradiation will therefore contain the products that form when vacancies, interstitials and $C_i$ form when reacting with each other ($V_2$, $C_iC_s$,) and with impurities in the lattice (VP, VO, $C_iP_s$) [15].

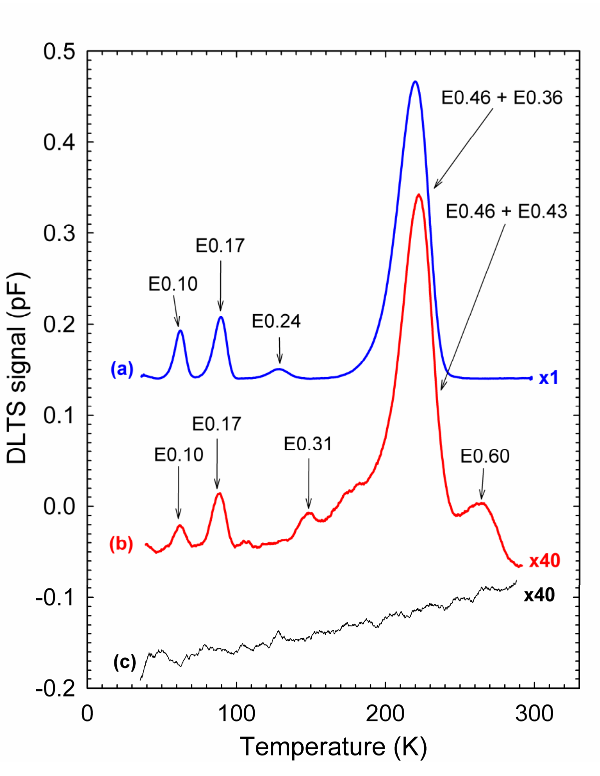



**Figure 5**: DLTS spectra of EPI n-Si: (a) Irradiated with MeV electrons; (b) Pt Schottky diode deposited by EBD, (c) control spectrum of resistively deposited Schottky diode.

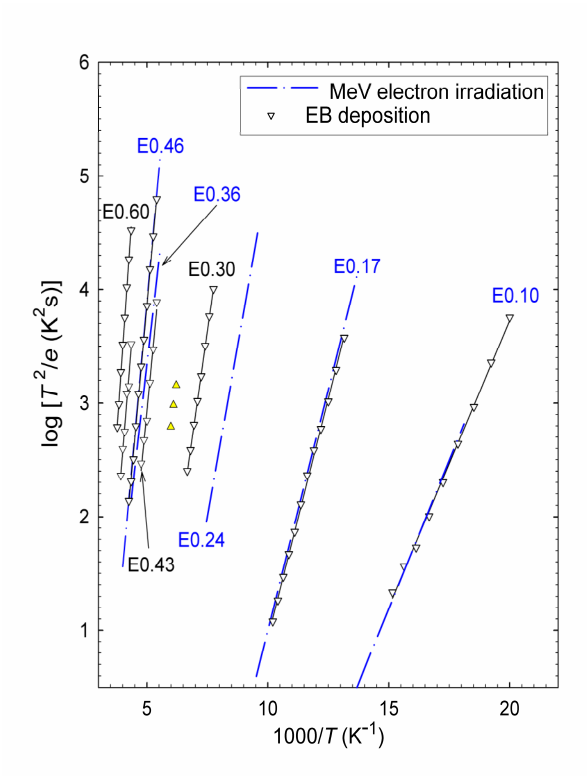



**Figure 6**: Arrhenius plots for defects introduced by: MeV electron irradiated n-Si (blue dot-dash line); and electron beam deposition (down triangles).

Curve (a) in Fig. 5 is the DLTS spectrum of MeV electron irradiated EPI n-Si recorded directly after irradiation with a fluence of $10^{15}$ $e^-$ $cm^{-2}$. It contains at least four DLTS peaks. From the Arrhenius plots where the signatures of these defects were determined (Fig. 6), these peaks are identified as E0.10 ($C_i$), E0.17 (superposition of A-center (VO) and $C_iC_s$), E0.24 ($V_2^{=/-}$) and the superposition of E0.46 + E0.36 [13]. Here the E0.46 and E0.36 contributions to the peak at 220 K were determined by high resolution Laplace DLTS measurements. E0.46 is the VP or E-centre, while E0.36 has a similar signature as one of the metastable components of the $C_iP_s$ centre [17]. The concentration ratio of VP to E0.36 is about 5:2. The VP + E0.36 peak also contains a small contribution due to the $V^{-/0}$ but this is too small to be distinguished from the two main peaks (VP and E0.36).

The DLTS spectrum recorded from Pt Schottky contacts that were fabricated by EBD, without any intentional shielding, is shown in curve (b) of Fig. 5. The similarities between some of the defects introduced by EBD and by MeV electron irradiation are evident. Both processes introduce E0.10 ($C_i$), E0.17 (VO + $C_iC_s$) and E0.46 (VP) [13 – 17]. This correspondence is confirmed by the Arrhenius plots in Fig. 6. From the Laplace DLTS spectra it was found that EBD does not introduce the E0.36 defect, but instead a defect peak E0.43 of which the DLTS peak also overlaps with that of the E0.46 (VP) peak. From the spectra in Fig. 5 it is also evident that EBD introduces at least two other defects not seen after MeV electron irradiation: E0.30 (similar, but not the same, signature as VOH [19]) and a defect E0.60. This latter defect consists of two closely spaced levels (see the Arrhenius plots in Fig. 6). This defect was also not observed in all EBD samples. It is also noteworthy that no divacancies ($V_2^{=/-}$) in measurable concentrations could be detected in samples prepared by EBD. Previously, a defect with very similar properties to $V_2^{=/-}$ was reported to be introduced after EBD of metal contacts on CZ Si [5].

## 4. Conclusions

Pt Schottky barrier diodes were fabricated onto n-Si(100) using electron beam deposition. The behaviour of the Schottky barrier diodes (SBD) was investigated under various annealing conditions. The variation of SBH and ideality factor with annealing temperature can be attributed to interfacial reactions of Pt and n-Si(100) and the subsequent formation of platinum silicides. The electrical properties of the Pt Schottky barrier diodes revealed the as deposited ideality factor of 1.02 and SBH of 0.80 eV. $Pt_2Si$ was formed at temperatures between 210°C and 280°C with ideality factor increasing to 1.16 and SBH decreasing to 0.77 eV. At 300°C, PtSi has formed increasing the ideality factor to 1.83 while the SBH decreased to 0.70 eV. DLTS revealed that electron beam deposition introduced defects which were identified as the E-centre (VP centre), the A-centre (VO centre), the interstitial carbon ($C_i$) and the interstitial carbon-substitutional carbon ($C_iC_s$) pair.

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