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Thermal stability of Co, Ni, Pt or Ru Schottky contacts on n-Si and defects introduced thereon during contacts fabrication using electron beam deposition

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Abstract

When using Schottky barrier diodes (SBDs) on silicon (Si) to study the thermal stability of radiation-induced defects, point defects injection into the silicon substrate can occur at temperatures where silicidation occurs. These injected point defects can react with the radiation-induced defects and may lead to an incorrect picture of annealing studies of these defects. In order to overcome this problem, we have annealed (1) ruthenium (Ru), cobalt (Co), nickel (Ni) and platinum (Pt) SBDs to form stable silicides on phosphorus (P) doped Si and (2) have measured the electrical characteristics of defects introduced during diodes fabrication by electron beam deposition (EBD), using conventional and (high resolution) Laplace (L-) deep level transient spectroscopy (DLTS). A primary electron trap at 0.48 eV below the conduction band was observed after EBD processing of the contacts. Isochronal annealing of the SBDs at 350 °C, annealed-in defects 0.05, 0.09, 0.18 and 0.28 eV below the conduction band. All the EBD-induced defects were removed after annealing at 600 °C. Primary defect depth profile versus annealing temperature results are also presented in this study.

Article Outline

1. Introduction

Silicides are an important integral for the VLSI circuits among many other applications. Due to very high melting point of some metals, the electron beam deposition (EBD) process is employed for the contact fabrication before the silicidation process. Several workers have shown that EBD can induce electrically active defects in the semiconductor bandgap when used to fabricate Schottky barrier diodes (SBDs) [1] and [2].

When using SBDs to study the thermal stability of radiation-induced defects, point defects injection into the Si can occur at temperatures where silicidation occurs [5]. These point defects can react with the radiation-induced defects and may lead to an incorrect picture of the annealing behavior of these defects. Therefore, to standardize the study of radiation-induced defects, a complete annealing study, establishing the removal of all the EBD-induced defects, is necessary. The silicide formation is also a necessary and important intermediate step.

2. Experimental procedure

In this study metal contacts, 100 nm thick each were fabricated, though a circular contact mask, using EBD for (1) Co, Pt or Ru and vacuum resistive deposition and for (2) Ni SBDs, onto P-doped Cz grown Si with a carrier concentration of 5.0×10^{16} cm^{-3}.

Prior to contact fabrication, the substrates were chemically cleaned, (i.e. degreasing, isochronal anneal at 300 °C in Ar for 10 min, immersing in dilute HF, then blow drying in N_2). The silicide formation and EBD-induced defects were electrically characterized by current–voltage (*I*–*V*), capacitance–voltage (*C*–*V*), (C-) and Laplace deep level transient spectroscopy (L-DLTS) [3] and [4] measurements on the Schottky contacts. The electrical characterization was repeated after every annealing cycle in Ar gas for 30 min between 100 and 600 °C in steps of 100 °C, to investigate the silicide formation and defect annealing behavior.

The defect '*signatures*' (i.e. energy position in the bandgap relative to the conduction band, E_T, and apparent capture cross-section, σ_a) were determined from the Arrhenius plots of $\ln(T^2/e_e)$ versus $1000/T$, where e_e is the electron emission rate and T is the measurement temperature.

The defect depth profiles (i.e. concentration versus depth) were obtained from DLTS pulse height measurements at a fixed temperature. The steady-state reverse bias voltage was kept constant while gradually increasing the majority carrier pulse. The depth profile was then extracted from dependence of DLTS signal on the pulse amplitude.

3. Results and discussion

In this section, we discuss the electrical characterization of the defects that are introduced by metallization using EBD method on the Si substrate. We will also discuss the silicide formation for Co, Ni, Pt, and Ru metal contacts.

3.1. Metal silicides formation

We have determined Co, Ni, Pt or Ru silicide formation from the graphs of Schottky barrier height versus annealing temperature (Fig. 1). The Schottky barrier height was extracted from *C*–*V* and *I*–*V* measurements. The Ni silicide, NiSi formed between 400 and 500 °C graph (a) cobalt silicides, CoSi and $CoSi_2$ formed between 100 and 300 °C graph (b), the ruthenium silicide, $RuSi_2$, formed at 100 °C graph (c) while it was observed from graph (d) that PtSi started forming at 200 °C. The results show that most of the silicides studied in this work are formed below 300 °C, the temperature at which the E-center anneals out. It has been suggested that the silicide formation causes the injection of vacancies into the semiconductor bulk [5] and this should contribute to the formation of the E- and A-centers

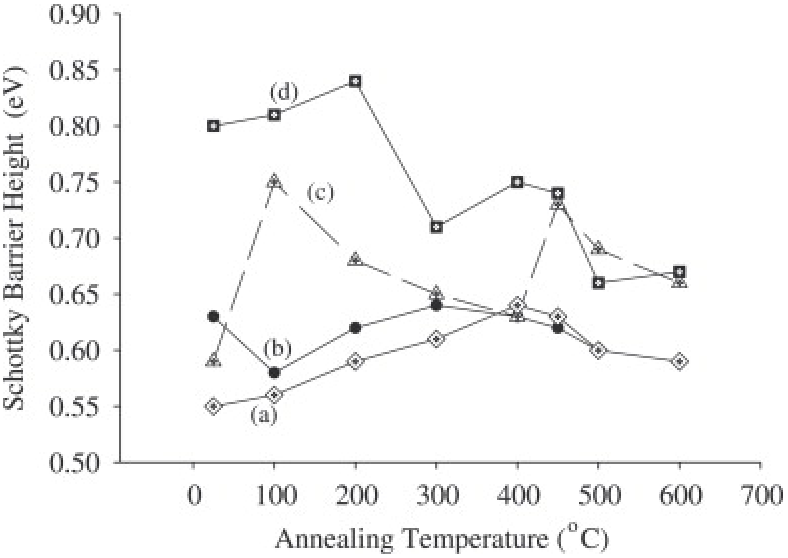

Fig. 1. Schottky barrier height against annealing temperature for (a) Ni, (b) Co, (c) Ru and (d) Pt Schottky contacts, obtained from *I–V* and *C–V* measurements after each isochronal annealing step.

3.2. DLTS analysis of EBD-induced defects in n-Si

We have observed a dominant defect level, which we call EP(0.48), the so-called E-center in all the EBD samples, but no defect levels were observed in the vacuum resistive deposition, processed samples within the detectable limit of DLTS system. This confirms that the EBD induce electrically active defects, at and beneath the contact surface, which is in agreement with several authors [1] and [2].

A small low temperature peak was also observed, and we speculate that it might be EP(0.09) (Fig. 2(a)). The EP(0.48) is the dominant defect. All the measured defect '*signatures*' were obtained from the Arrhenius plots shown in Fig. 3 and the results are summarized in Table 1. The defect levels EP(0.05), EP(0.18), and EP(0.28) were all introduced after annealing at 350 °C, while EP(0.50) was observed after annealing at

450 °C. The origins of EP(0.05) and EP(0.50) are not clear at the moment but the '*signature*' of EP(0.18) is similar to V–O (A-center) [3], [6] and [7], EP(0.28) is the P_s–C_i center [8] and EP(0.48) is the well-known P–V (E-center). The E-center increased slightly in concentration after a 100 °C anneal and this may be due to the injected vacancies released when the Ru silicide starts forming. The A-center, was not observed in our as-deposited samples but only observed after annealing at 350 °C, graph (c). The E-center was completely removed after annealing at 300 °C and the sample was defect free after an annealing temperature of 600 °C.

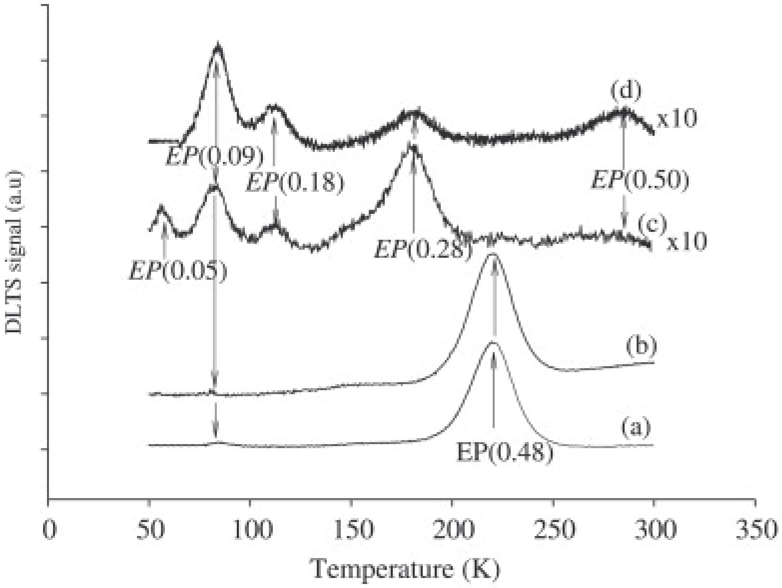

Fig. 2. The DLTS spectra of the EBD induced defects on Ru Schottky contacts on P-doped Si for (a) as-deposited, after annealing at (b) 100 °C, (c) 350 °C and (d) 450 °C. The DLTS were measured at a quiescent reverse bias of −2 V and pulse voltage 0 V and a rate window of 80 s^{-1}.

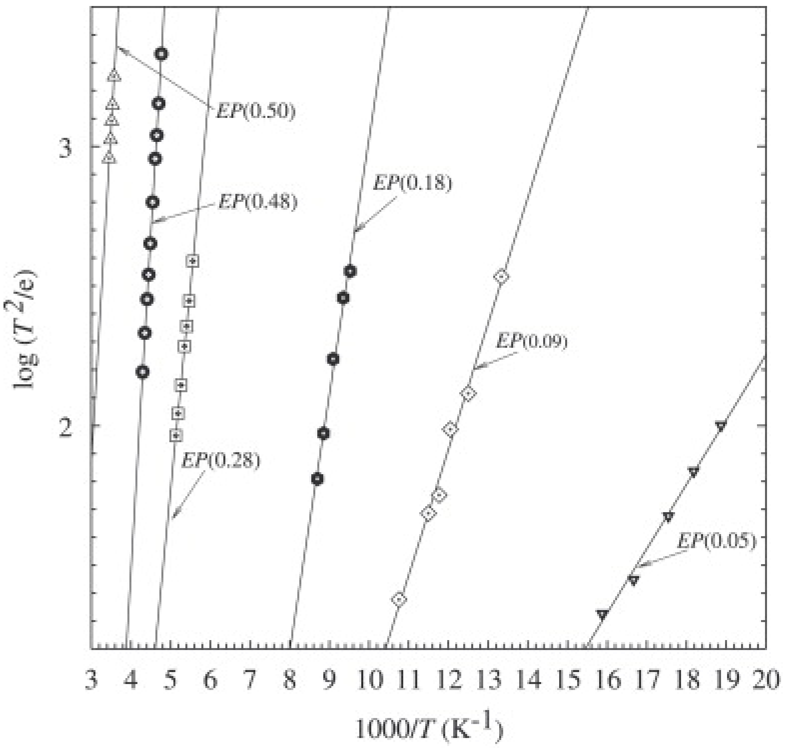

Fig. 3. An Arrhenius plot for EBD induced defects in P-doped Si after Ru Schottky diode fabrication by EBD process.

Table 1.

Summary of EBD induced defects in n-Si

Defect	**E_T (eV)**	**σ (cm^2)**	**T_P^{a} (K)**	**T_{out} (°C)**	**Origin**
EP(0.50)	0.50	3.7×10^{-18}	290	600	?
EP(0.48)	0.48	4.1×10^{-14}	220	300	P–V **[5]**
EP(0.28)	0.28	8.6×10^{-17}	180	600	P_s–C_i **[8]**
EP(0.18)	0.18	3.8×10^{-16}	110	600	V–O **[3]**, **[6]** and **[7]**
EP(0.09)	0.09	8.6×10^{-19}	85	600	C_s–Si_i ?
EP(0.05)	0.05	1.6×10^{-19}	60	450	?

[a] The peak temperature was measured at a rate window of 80 s^{-1}.

3.3. The depth profile of the E-center

The defect concentration depth profile for the E-center showed that the defect concentration decreases from the semiconductor surface as depicted in Fig. 4, and this proves that the energetic particles emerging from the filament during diode fabrication creates vacancies on and beneath the semiconductor surface. We have also compared the depth profiles for Ru and Pt Schottky contacts, graphs (a) and (b) in Fig. 4, respectively. The defect concentration at the semiconductor surface is higher for Ru than for Pt, and this can be attributed to the fact that Ru (melting point, 2250 °C) has higher melting point than Pt (melting point, 2041 °C), hence in Ru deposition the particles from the filament are more energetic than in Pt deposition (since a stronger field is used for the higher melting point material) therefore a larger defect concentration in Ru SBD samples.

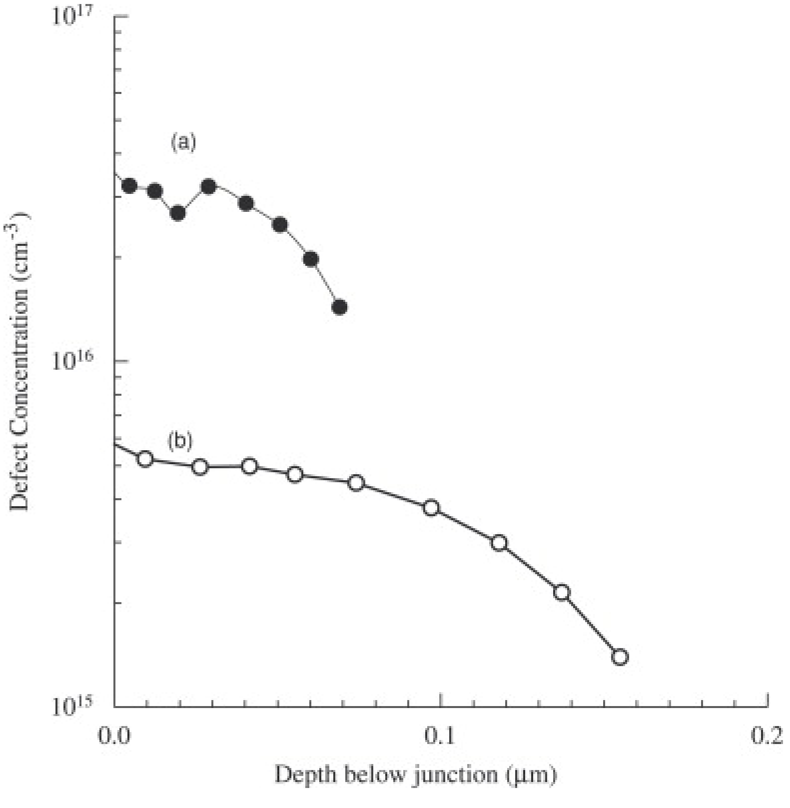

Fig. 4. Depth profile for the E-center in (a) Ru Schottky contacts and (b) Pt Schottky contacts on P-doped Si. These measurements were recorded at a quiescent reverse bias of −2 V.

The defect concentration profiles for the E-center as a function of annealing temperature for the Pt SBD is depicted in Fig. 5. The defect profile shows an increase in defect concentration deeper into the bulk material as the temperature is increased from room temperature (as-deposited) and after annealing at 100 and 150 °C. The E-center diffuses into the semiconductor as it become mobile at elevated temperatures before it dissociates. The reason why the profile is not flat as the annealing temperature increases is not clear at the moment.

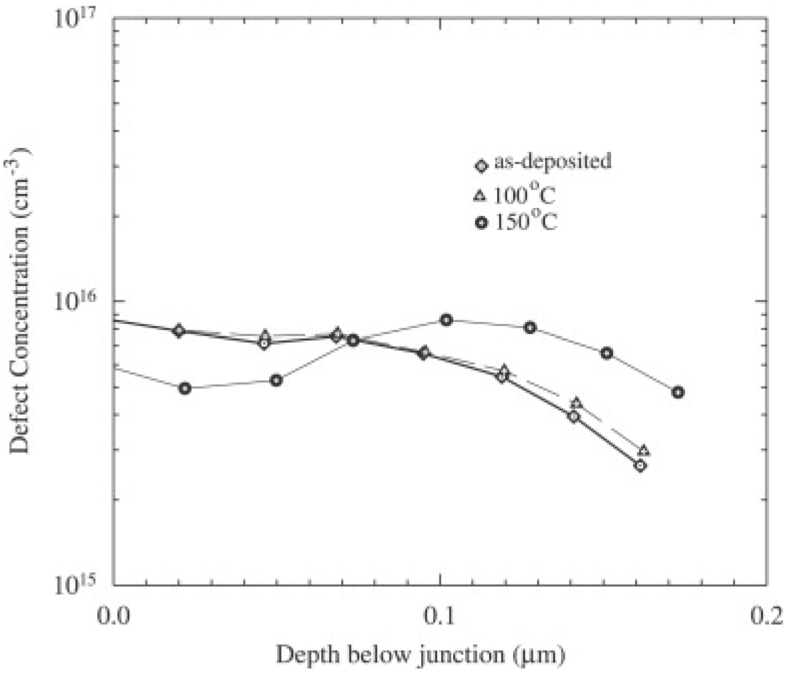

Fig. 5. Depth profile for the E-center in Pt for (a) as-deposited, and after annealing at (b) 100 °C and (c) 150 °C. These measurements were recorded at a quiescent reverse bias of −2 V.

4. Summary

We have established the silicide formation on n-Si using Ru, Co, Ni and Pt. Most of the silicides start forming at a lower annealing-out temperature of the E-center. We have also measured electron traps induced in P-doped silicon by EBD processing of Co, Ru or Pt SBD. The E-center was the dominant defect, but A-center and the divacancy were not observed in the as-deposited samples. There were no observable defect levels (within our experimental detection limit) in the control sample, where vacuum resistive deposition was the fabrication processing method, as expected. The secondary defect levels EP(0.05), EP(0.09), EP(0.18), EP(0.28) and EP(0.50) were observed after annealing at 350 °C, and a defect free depletion region was observed after annealing at 600 °C. The depth profile of the E-center, showed a decrease in concentration from the semiconductor surface into the bulk, an indication that this primary defect was radiation induced. The analysis of the depth profiles after annealing cycles showed that the E-center diffused into the semiconductor bulk as the temperature was increased.

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