JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 5 No 2, 02005(3pp) (2013)
ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 5 № 2, 02005(3cc) (2013)

Phase Transition Sensitive Schottky Barriers In Ga-Si(P) Contacts

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(Received 15 February 2013; revised manuscript received 03 May 2013; published online 04 May 2013)

Investigation and understanding of Schottky diodes continue to be interesting both for basic as well as technological points of view. Even now the evolutionary aspects of such contacts are not very clearly understood. In this paper it is shown that in respect of interfacial strain contribution to the barrier heights of such contacts semiconductor – liquid metal contacts are relatively better placed than solid semiconductor-solid metal contacts. Results on Ga-Si(p) contact are discussed in this paper to show phase sensitive contribution to the barrier height of such Schottky contacts.

Keywords: Schottky barrier, Phase transition, Barrier height, Ideality factor.

PACS numbers: 73.30. + y, 73.20. – r

1. INTRODUCTION

Metal-semiconductor (M-S) contacts have continued as an important and interesting field for investigations both from points of view of science and technology [1, 2]. In comparison to solid-solid M-S contacts, relatively fewer investigations have been reported for liquid metal semiconductor contacts. In earlier paper [3, 4] we had reported advantages of investigations on such contacts along with the results of our studies on stability aspects of such contacts of Schottky nature. It was shown that these contacts are fairly stable in their behaviour over a long period of time and thus show negligible ageing effect. Hence, these make themselves as suitable systems for closely looking at the evolutionary aspects of Schottky contacts. Here in this paper, we report results of our investigations on Schottky contacts between liquid gallium and silicon, especially around the melting point of gallium. It is shown that such contacts exhibit a phase transition sensitive characteristics around the melting point, driven by the interfacial strain. Imprint of this are seen in both I-V-T and C-V-T characteristics of such contacts.

2. EXPERIMENTAL

In this investigation *p*-type Si <100> crystals having acceptor density of around 10^{16} /cm^3 were used. The ohmic back contact on the rough surface of the silicon crystal was made of aluminium by depositing 0.15 μm thick film of pure aluminium by thermal evaporation in a vacuum of around 10^{-6} torr followed by thermal annealing at 500 °C for half an hour. The other polished surface of the crystal was etched in 1 : 3 : 5 mixture of electronic grade hydrofluoric acid, nitric acid and acetic acid for around 30 seconds when brown vapors appeared and then it was dipped for a minute in dilute solution of 1 : 9 hydrofluoric acid and deionised water. Finally it was thoroughly washed in deionized water and quickly dried. The crystal was then mounted in the sample holder [5] below the capillary arrangement and pure gallium (99.99 %) was put into the capillary using a disposable syringe. The I-V data on the formed Schottky diodes were obtained at 100 Hz and C-V data were obtained at 100 kHz using HP-LCR meter (Model-4274A) through a suitably developed software programme. The choice of 100 Hz for I-V data was made so that characteristics are near dc behavior and choice of 100 kHz for C-V data was made so that any interfacial capacitance due to interface charges etc. does not contribute significantly. Temperature variations were made by controlling the ambient room temperature of the AC room, housing the experimental arrangement, since the range of temperature variation for the present study is ten degrees only around the room temperature. The temperature near the Schottky contact was measured using a suitably placed thermometer with an accuracy of ± 0.10 °C.

3. RESULTS AND DISCUSSIONS

The I-V data on the Schottky contact at different temperatures (295 K, 297 K, 299 K, 302 K and 305 K) are shown in Fig. 1. From this figure, it can be observed that I-V characteristics of the Schottky contact around the melting point of gallium(302.750 K) is anomalous in the sense that there is a sharp deterioration in the rectifying nature near this temperature.

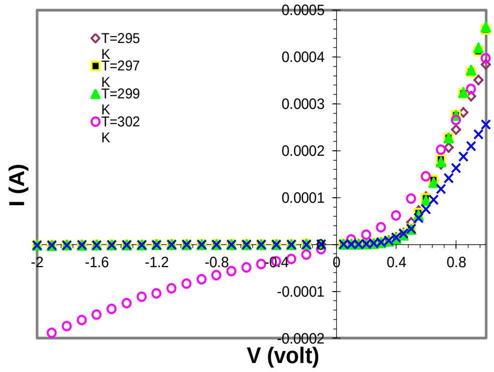

Fig. 1 – I-V characteristics of Ga-Si(p) diode at different temperature around melting point of gallium

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Otherwise, the rectification behavior at other temperatures is quite good. To highlight this and to see this more closely, both forward and reverse bias data have been plotted as a function of temperature at some fixed but different values of forward and reverse biases. These are shown in Fig. 2. The anomalous behaviour around the melting point of gallium is quite prominently exhibited by this figure and is seen to be centered in a narrow temperature region around the melting point of gallium (302.75 K).

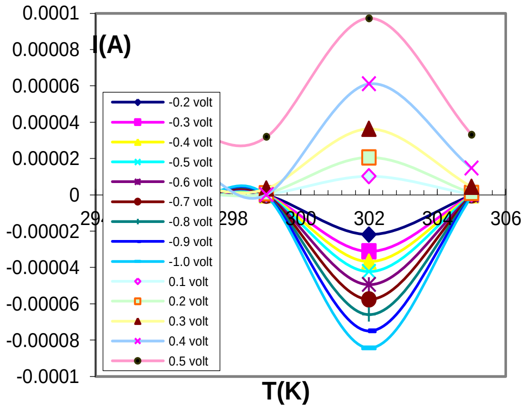

Fig. 2 – I-T Characteristics of Ga-Si(p) Schottky diode at different voltages before correction

The equivalent circuit of a practical Schottky diode generally includes a series and a shunt resistance besides a capacitance in parallel to the junction. The presence of series and shunt resistances can affect the measured I-V data as pointed in our earlier paper [3]. Therefore, more realistic I-V characteristics were obtained after corrections made as discussed earlier and the resulting I-T characteristics at different biases is shown in Fig. 3. This shows that the observed anomaly is true one in the present case although its observed magnitude is reduced by presence of these parasitic components.

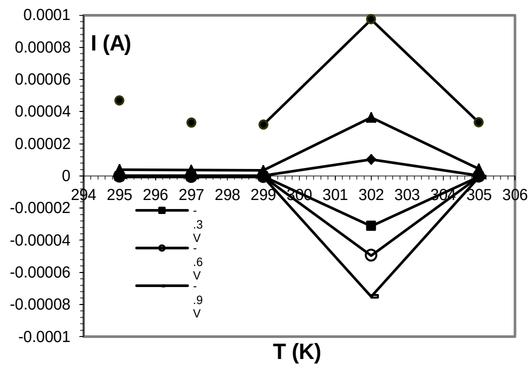

Fig. 3 – I-T Characteristics of Ga-Si(p) Schottky diode at different voltages after correction

The C-V-T data obtained on the Schottky contact was plotted (Fig. 4) to show variation of capacitance with temperature at fixed biases. From here it can be seen that there is significant change in the trend of variation in the magnitude of exhibited capacitance values.

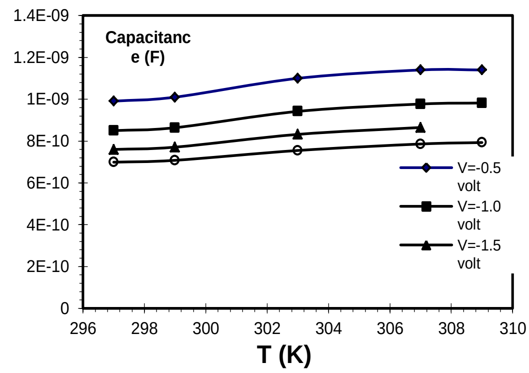

Fig. 4 – Capacitance vs Temperature of Ga-Si (p) Schottky diode at different voltages

To make it more apparent, the rate of change of capacitance values at these different fixed biases were plotted. This is shown in Fig. 5. It is seen that a similar kind of anomaly as seen in current voltage characteristics around melting point of gallium is also visible in the capacitance voltage characteristics.

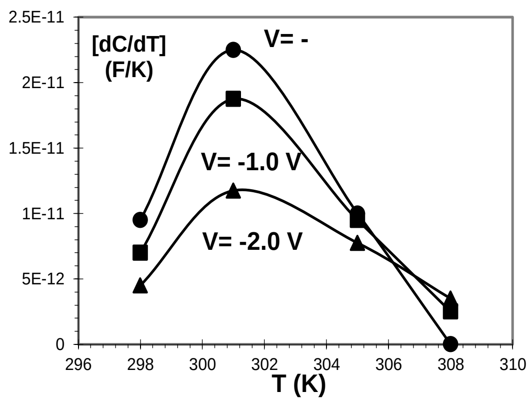

Fig. 5 – (d*C*) / (d*T*) (F / K) vs Temperature of Ga-Si(p) Schottky diode at different voltages

I-V-T and C-V-T behaviour of Schottky contacts originate from interfacial dipole layer characteristics and charge transport mechanisms through it [6]. As far as charge transport in the present case is concerned, it is thermionic emission. Such an inference is based on:

– the doping density in the semiconductor used (silicon in the present case) is not high and the temperature at which characteristics are being observed is not very low to warrant tunneling as the dominating charge transport mechanism,

– the characteristics energy E_{00}, as calculated in present case, is not of the order of kT to warrant thermionic field emission as dominant charge transport mechanism. On the contrary E_{00} is more than ten orders lower than kT as required for identifying ther-mionic emission as dominant charge transport mechanism.

Analyzing the observed behaviour on such basis shows that the ideality factor is around 1.1 at all temperatures. However, the flat band barrier height and built in potential show a decrease near the melting point of gallium Fig. 6.

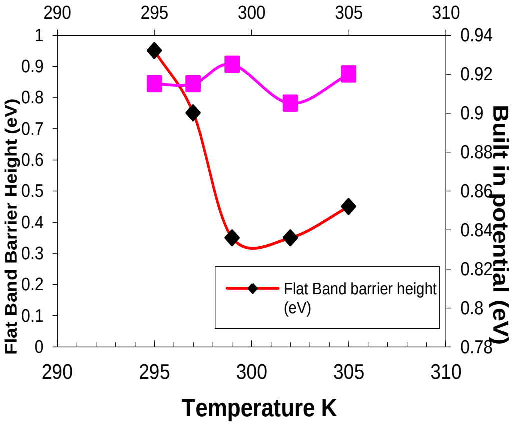

Fig. 6 – Flat band barrier height and built-in volt potential variation with temperature for Ga-Si(p) diode

It has been reported in the literature [7-9] that the Schottky diode behaviour in general have contributions both from the bulk materials used in the contact as well as their interface. Therefore, it can be thought that the observed anomaly around the phase transition of gallium is driven by changes in the bulk properties of gallium or its interface with silicon, since the bulk properties of silicon are not expected to show any significant change around this temperature. Moreover, the contact with liquid gallium has been made immediately on the cleaned and etched silicon surface leaving little time for formation of oxide layer of any significant thickness.

Melting/solidification of a substance is a phase transition of the first kind. It is seen that in such phase transitions there is a rearrangement of crystal lattice of the substance consisting of changes in the interatomic distances and the angle between lattice planes. As a result the symmetry of the substance changes discontinuously. At the same time there is a discontinuous change in the volume and density as well. There is also a change in the internal energy accompanied by evolution or absorption of heat energy, which is known as latent heat of transition and does not appear as an apparent change in the temperature of the substance. All this occurs over a narrow range of temperature centered on the phase transition temperature. The thermodynamic conditions of equilibrium for these kinds of discontinuous changes between phases of different symmetry require that such transitions occur at constant temperature and pressure. But in processes occurring at constant pressure the quantity of heat absorbed by the body is equal to change in its heat function and consequently the entropy also undergoes a change during such phase transitions. Analyzing the effect of this kind of changes in the internal energy of bulk gallium on the saturation current and consequently on the barrier height, it is found that it is negligible as compared to the observed changes. This is also certified by the fact that no anomalous change in the resistivity of gallium has been reported around the melting point of gallium [10]. Moreover, it has also been reported that structural disturbances set-in very slowly in gallium on melting. It has also been reported [11] from the structure-factor variation study across the melting point of gallium that the number of nearest neighbors and the sphere of first coordination remain almost unchanged over a temperature range of 203 K to 323 K. Therefore, it seems that the observed anomaly originates predominantly from changes at the interface around the melting point of gallium and not from changes in the bulk properties of gallium. It may be noted that in case of solid-solid interface Schottky diodes, the contribution from interface is usually masked by the contributions from the bulk unless the thickness of metallic over layer coverage is few mono layers only. Exceptions to this have been reported rarely [7, 8].

Interfacial changes near the phase transition temperature are likely to give rise to build up or relaxation of bonds between gallium and silicon – while silicon has cubic structure, gallium in the solid state has orthorhombic structure [12, 13]. Thus, interfacial strain can be expected to give rise to interface states and their additional creation may modify Fermi levels at the interface, interfacial band alignment and the barrier height [14-16]. Obviously, the quantum of changes in the barrier height may be expected to depend on both the density of original interface states existing on the semiconductor and the density of interface states arising from interfacial strain. Therefore it can be concluded that the evolutionary aspects of Schottky diodes e.g. contribution of interfacial strain which are seen only at smaller thicknesses of metallic over layers in case of solid-solid contacts may be seen more clearly in case of solid-liquid contacts.

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