

The Effect of Sintering Temperature on the Barrier Height of p-type PtSi Schottky Diodes

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Abstract

The effect of sintering temperature on the barrier height of p-type PtSi Schottky diodes is studied by electrical and infrared photoresponse methods. It is revealed that there is a consistent difference of about 0.06 eV for two samples sintered at different temperatures.

1. Introduction

Ever since higher infrared (IR) responsivity was successfully demonstrated in Schottky diodes having very thin metal layers by Archer and Cohen (1973), there has been increasing interest in utilising these low barrier height Schottky diodes for IR detection (see e.g. Elabd and Kosonocky 1982; Shepherd 1987, 1988). For IR applications, the cutoff wavelength of IR response is given by

$$\lambda_{\text{cutoff}} = 1.24/\phi_b, \quad (1)$$

where λ_{cutoff} and the barrier height ϕ_b are in microns and electron volts respectively. To achieve a longer IR photoresponse cutoff, the Schottky barriers have to be optimised for low barrier heights. To achieve this, Schottky diodes are usually fabricated on p-type Si substrates.

Metal-silicides formed by noble metals such as palladium, platinum and iridium on n-type silicon substrates, giving barrier heights of 0.77, 0.87 and 0.93 eV respectively, have been well documented by several workers (Tu *et al.* 1981; Murarka 1980; Wagner *et al.* 1983). The variation of the effective barrier height on n-type Si for these materials due to different experimental conditions, parameters and techniques has also been extensively studied (Köster *et al.* 1977; Eizenberg *et al.* 1981; Lew and Helms 1984; Chin-An 1985). However, no similar data on the effects of sintering temperature on p-type PtSi Schottky diodes are currently available. Hence, the aim of this short paper is to present the findings on p-type PtSi Schottky barrier diodes fabricated at two different sintering temperatures.

2. Fabrication of the Devices

The samples used in this study were fabricated on p-type Si, with (100) orientation and $10\ \Omega\text{cm}$ resistivity. Prior to Pt deposition, the substrates were treated to standard Si cleaning, including RCA2 Caro's etch follow by deionised water etc. The Pt deposition was done by using e-beam evaporation in a vacuum of the order of 10^{-6} Torr (1 Torr \equiv 133 Pa). In order to optimise IR detection in the 2 to $3\ \mu\text{m}$ region, optical cavities were formed by silicon monoxide (SiO) evaporation on the front and the back side of the wafer, and about 4 nm of Pt was deposited at room temperature onto the substrates giving a PtSi thickness of about 7 nm (Murarka 1983). The thickness of the evaporated Pt and the dielectric (SiO) were measured with a quartz crystal oscillator. The SiO thickness was also monitored with a laser ellipsometer to calibrate the quartz oscillator measurements.

Type A Schottky diodes were formed by sintering in the furnace under foaming gas (mixture of 4% H_2 and 96% N_2) at 350°C for a total of 40 minutes. In addition to this sintering at 350°C , type B Schottky diodes were sintered at a higher temperature of 475°C for a further 20 minutes under the same conditions. This is therefore the only difference between the type A (established earlier by Chin *et al.* 1990a, 1990b) and type B Schottky diode fabrication processes. All possible excess Pt was etched away with *Aqua Regia*. The areas of the Schottky diodes are 2.7×10^{-4} and $5.0 \times 10^{-5}\text{ cm}^2$ for type A and type B respectively. However, it is not expected that this difference would have any effect on the forward I - V and IR photoresponse measurements since guard rings are fabricated around each device to minimise leakage current and avoid premature breakdown. A reverse breakdown in excess of 50 V (defined as $1\ \mu\text{A}$ of current flowing or greater) has been achieved for some of the working type A devices (Chin *et al.* 1989). Electrical connections were made by aluminium deposition on the back of the wafer. The detailed fabrication procedure for the devices utilised here can be found in Chin (1990).

3. I - V and IR Photoresponse Results and Discussion

Due to the excessive thermal current at room temperature, forward I - V and infrared photoresponse measurements were performed at or near liquid nitrogen temperature. Three samples each from the two different sintering temperatures were measured. Fig. 1 shows the forward I - V characteristics of typical type A and B diodes at 77 K. The zero bias barrier heights ϕ_{b0} were evaluated from thermionic emission theory using the usual approach (Sze 1981), i.e.

$$\phi_{b0} = \frac{kT}{q} \ln \left(\frac{A^{**}T^2}{J_s} \right), \quad (2)$$

where k is Boltzmann's constant, T is the temperature in Kelvin, q is the electronic charge and J_s is the saturation current density at zero bias. The effective Richardson constant A^{**} used in the evaluation of the zero bias barrier height was $32\text{ A cm}^{-2}\text{ K}^{-2}$ (Sze 1981). Average barrier heights of 0.235 ± 0.010 and $0.290 \pm 0.010\text{ eV}$ were calculated from each of the three samples for type A and B respectively. The type A and B samples were observed to differ

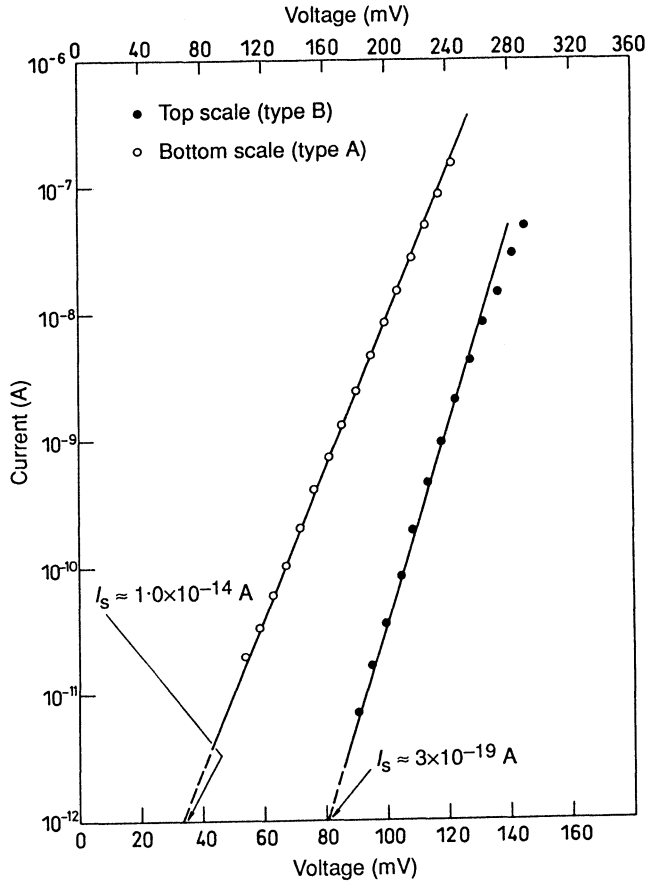


Fig. 1. Forward I - V characteristics of a type A and B PtSi Schottky diode measured at or near liquid nitrogen temperature.

in barrier height by approximately 0.055 eV. It was also determined that a reverse breakdown in excess of 35 V occurred for the type B Schottky diodes.

IR photoresponse measurements were made on both diodes at 78 K and at a reverse bias of 2.0 V. The Schottky diodes were backside illuminated (i.e. from the Si side) so that photons with energy higher than the bandgap of Si (i.e. with a wavelength shorter than $1.1 \mu\text{m}$) were absorbed in the bulk Si. The results of the IR photoresponse measurements are presented in Fig. 2 for typical type A and type B samples. Here the square root of the photoyield per incident photon $(Yh\nu)^{1/2}$ is plotted as a function of photon energy. According to Sze (1981), extrapolation of the curve to the photon energy axis yields directly the photoemission barrier height, termed the optical barrier. A barrier height of 0.235 eV for a type A Schottky diode was extracted from this plot. The IR responsivity for type B is very low and not as well correlated as type A. Nevertheless, the optical barrier height can be estimated to be roughly 0.30 ± 0.05 eV. (Note that the datum point at 0.41 eV is ignored in this linear fit.) The results obtained from IR photoresponse measurements of type A Schottky diodes also show a lower barrier height than type B diodes, in agreement with the I - V data described earlier.

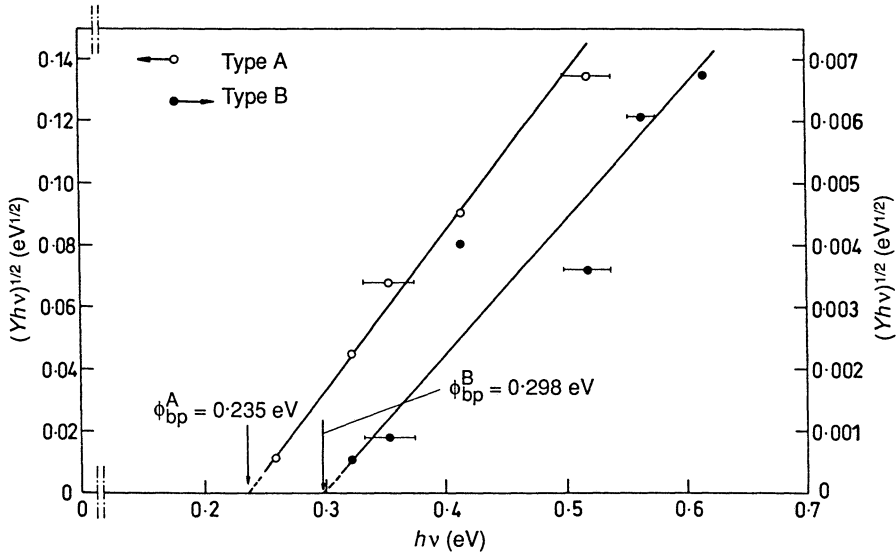


Fig. 2. Square root of the photoyield per incident photon as a function of photon energy, also known as Fowler's plot.

Two possible causes of this behaviour are now considered. While the fundamental properties determining the height of the Schottky barrier and the formation of Schottky diodes are still not understood, there are grounds for expecting the sum of the n-type and p-type barrier heights to add up to the energy bandgap (Rhoderick 1970; Cowley and Sze 1965). In addition, previous work suggests that this is a reasonable approximation for Si (Smith and Rhoderick 1971), GaAs (Missous *et al.* 1986; Chin *et al.* 1990c) and InP (Chin *et al.* 1990c).

Based on the above reasoning, it is expected that the n-type barrier height for the corresponding type A diode is around 0.88 eV, which is in agreement with the reported value for an n-type PtSi Schottky diode (Rhoderick and Williams 1988). As for type B, the n-type barrier height would be around 0.83 eV. This appears to correspond closer to the Pt₂Si Schottky diode, which according to Murarka (1980) and Freeouf (1981), has a barrier height in the range 0.78–0.82 eV. Thus, it is possible that type B is a Pt₂Si Schottky diode. However, in the absence of extensive surface studies of the type B Schottky diodes, such a conclusion cannot be drawn and this explanation must therefore be considered unproven. Nevertheless, a recent study by Chen *et al.* (1989) using transmission electron and X-ray diffraction lends some support to this hypothesis. Pt thin films with thicknesses 5–30 nm were deposited at 450°C onto a p-type <111> oriented Si wafer. We observed β -Pt₂Si in these samples with 5 and 20 nm thick Pt films, but with different orientations. However, a sample deposited with 30 nm Pt showed the formation of a PtSi epitaxial layer and polycrystalline Pt with the polycrystalline texture being that of α -Pt₂Si.

Another possible explanation for the behaviour observed in the present diodes has been offered by Chino (1973), Card (1975) and Basterfield *et al.* (1975) who observed the Al–Si Schottky diode under heat treatment. When the Al–Si system on n-type substrate is heated to near 500°C, the Si is taken

into solution with the Al. On cooling, some of the dissolved Si recrystallises and leads to the formation of a thin p-doped layer (because Al is an acceptor) at the interface, which increases the barrier height. Although lower solid solubility is expected from the Pt-Si system, a similar mechanism can still occur. However, Pt is a donor instead of an acceptor (unlike Al), and therefore the 'opposite' will occur, i.e. the barrier will increase when the thin n-doped Si layer forms at the interface as the system cools.

4. Summary

The barrier heights of p-type (100) PtSi Schottky diodes fabricated by sintering the samples at two different temperatures were evaluated using electrical forward I - V and IR photoresponse experimental techniques. From both experiments, it was found that the type A barrier height (0.235 eV) is substantially and consistently lower than the type B barrier height (0.290 eV) by about 0.06 eV.

For IR detection applications, it is important to have low barrier height and high IR responsivity. Hence, it is obvious that IR detectors should be fabricated in accordance with type A Schottky diodes, giving a cutoff wavelength of $5.3\text{ }\mu\text{m}$ at a reverse bias of 2 V (according to equation 1) and a Schottky emission coefficient of about $0.5\text{ eV}^{-1/2}$ (slope of type A diode in Fig. 2).

The possible mechanisms of this behaviour are postulated. In order to determine the exact causes of the effect, further detailed study of the surface structure of the devices is necessary.

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References

- Archer, R. J., and Cohen, J. (1973). Schottky barrier IR detector having ultra thin metal layer, U.S. Patent No. 3757123.
- Basterfield, J., Shannon, J. M., and Gill, A. (1975). *Solid-State Electron.* **18**, 290.
- Card, H. C. (1975). *Solid-State Commun.* **16**, 87.
- Chen, J. R., Chang, L. D., and Yeh, F. S. (1989). *J. Vac. Sci. Technol. A* **7**, 1345.
- Chin-An, C. (1985). *J. Appl. Phys.* **58**, 1412.
- Chin, V. W. L. (1990). Unpublished Ph.D. Thesis, University of New South Wales.
- Chin, V. W. L., Storey, J. W. V., and Green, M. A. (1989). *Solid-State Electron.* **32**, 475.
- Chin, V. W. L., Green, M. A., and Storey, J. W. V. (1990a). *Solid-State Electron.* **33**, 299.
- Chin, V. W. L., Storey, J. W. V., and Green, M. A. (1990b). 'Characteristics of p-type PtSi Schottky diodes under reverse bias. *J. Appl. Phys.* (in press).
- Chin, V. W. L., Green, M. A., and Storey, J. W. V. (1990c). *J. Appl. Phys.* **68**, 3470.
- Chino, K. (1973). *Solid-State Electron.* **16**, 119.
- Cowley, A. M., and Sze, S. M. (1965). *J. Appl. Phys.* **36**, 3212.
- Eizenberg, M., Foell, H., and Tu, K. N. (1981). *J. Appl. Phys.* **52**, 861.
- Elabd, H., and Kosonocky, W. F. (1982). *RCA Rev.* **43**, 571.

- Freeouf, J. L. (1981). *J. Vac. Sci. Technol.* **18**, 910.
- Köster, U., Tu, K. N., and Ho, P. S. (1977). *Appl. Phys. Lett.* **31**, 634.
- Lew, P. W., and Helms, C. R. (1984). *J. Appl. Phys.* **56**, 3418.
- Missous, M., Rhoderick, E. H., and Singer, K. E. (1986). *Electron. Lett.* **22**, 241.
- Murarka, S. P. (1980). *J. Vac. Sci. Technol.* **17**, 775.
- Murarka, S. P. (1983). 'Silicides for VLSI Applications' (Academic: New York).
- Rhoderick, E. H. (1970). *J. Phys. D* **3**, 1153.
- Rhoderick, E. H., and Williams, R. H. (1988). 'Metal-Semiconductor Contacts', 2nd edn (Clarendon: Oxford).
- Shepherd, F. D. (1987). *SPIE IR Detector* **443**, 42.
- Shepherd, F. D. (1988). *SPIE IR Detectors Arrays* **930**, 2.
- Smith, B. L., and Rhoderick, E. H. (1971). *Solid-State Electron.* **14**, 71.
- Sze, S. M. (1981). 'Physics of Semiconductor Devices', 2nd edn (John Wiley: New York).
- Tu, K. N., Thompson, R. D., and Tsaur, B. Y. (1981). *Appl. Phys. Lett.* **38**, 626.
- Wagner, L. F., Young, R. W., and Sugarmann, A. (1983). *IEEE Electron. Dev. Lett.* **EDL-4**, 320.

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