Thermal Stability of Re Schottky Contacts to 6H–SiC

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***Abstract*—The thermal stability of a 100-nm thick sputter-deposited Re film as contact to 6H–SiC was studied by backscattering spectrometry and by measurements of the forward current–voltage (*I–V*) characteristic. The initial Schottky barrier height of 0.71 eV and ideality factor of 1.6 change after 2 h of annealing in vacuum at 700 °C to 1.04 eV and 1.1, respectively. They remain stable after annealing for additional 2 h at that same temperature. The initial change is attributed to a recovery of sputter damage in the SiC. The observed stability of the Schottky barrier is attributed to the thermodynamic stability of Re with SiC, as confirmed by the unchanging backscattering depth profiles. After annealing at 900 °C, the Schottky barrier becomes unstable although no interaction between the Re film and the SiC substrate is detectable in the depth profiles.**

***Index Terms*—Annealing, Schottky barrier, sputtering.**

I. Introduction

Rhenium is the only known metal that is thermodynamically stable in contact with SiC, i.e., Re has a tie-line to SiC in a ternary Si–C–Re phase diagram [1]. The stability of Re thin films on 3C–SiC up to 1100 °C was experimentally confirmed in a study by Chen *et al.* [2]. This stability makes Re an interesting candidate for a stable Schottky contact in high-temperature applications. However, chemical stability is too crude a guide to ensure the stability of the electrical characteristics of the contact. The present study aims at evaluating the thermal stability of the Schottky barrier height of sputter-deposited Re contacts to n-type 6H–SiC.

II. Experimental Details

The 6H–SiC wafer (CREE Research, Inc.) used in this work was n-type, 280 μm thick, with a 10 μm-thick n-type epilayer grown on its Si face. The substrate and the epilayer were doped with nitrogen to levels of $7.3 \times 10^{17}/\text{cm}^3$ and $1 \times 10^{16}/\text{cm}^3$, respectively. Prior to deposition, the samples were degreased in organic solvents in an ultrasonic bath (trichlorethylene, acetone, and methanol, sequentially). Circular diodes of three different diameters (0.05, 0.1, 0.25 cm) were fabricated by photolithographic patterning and lift-off. Immediately before the deposition the samples were etched in an aqueous solution of 10% HF for 10 s and then blown dry with N_2 gas.

The Re films were deposited in an rf-sputtering system (base pressure of 4×10^{-7} torr) using a planar magnetron cathode of 7.5 cm in diameter. The substrate holder was placed 7 cm below the target and was neither cooled nor heated externally. Rhenium films were deposited under a total pressure of 5 mtorr and at 200 W rms from an elemental target. Post-deposition annealing was done in an evacuated tube furnace (5×10^{-7} torr). Samples for backscattering analysis were processed concurrently with the diode samples.

The forward current-voltage (*I–V*) characteristics, were measured at room temperature with a HP-4145A parameter analyzer. An indium-gallium alloy was pasted on the backside of the sample as a back contact to the heavily doped substrate. Lien's method [3] was employed to determine the series resistance, R, from each *I–V* characteristic, followed by a least-squares fit on a log-linear scale of the I versus V–IR plot to obtain the saturation current density, J_s, and the ideality factor, n. With the saturation current density thus established, and assuming the thermionic emission model, the barrier height was calculated from the equation [4]

$$\Phi_B = \frac{kT}{q} \ln\left(\frac{A^{**}T^2}{J_s}\right)$$

where $A^{**} = 72$ A/cm^{2}K^2 is the effective Richardson constant for 6H–SiC [5]. In all samples, it was verified that the current scaled with the area of the diode. This proves that it is the metal/epilayer interface that determines the *I–V* characteristics (and not the back contact), and that the current is not due to a peripheral leakage but flows across the area of the contact.

The Schottky barrier height and the ideality factor of individual diodes were extracted from *I–V* measurements before and after thermal annealing. Nonpatterned samples were characterized by 2 MeV 4He^{++} backscattering spectrometry to determine compositional profiles and monitor interactions in the samples.

III. Results and Discussion

Fig. 1 shows backscattering spectra of a 100-nm thick Re film on 6H–SiC before and after 1 h annealing in vacuum at 900 °C. The spectra overlap within experimental accuracy, which is consistent with the thermodynamic stability of Re and 6H–SiC. Within the depth resolution of this technique (≈10 nm) no interfacial instability can be detected either.

In contrast to the backscattering spectrometry results, the *I–V* characteristics do change upon annealing. Fig. 2 shows the *I–V* characteristics of the contacts before and after various heat treatments. An exponential behavior is observed in all cases with an ideality factor of 1.6 for as-deposited Re and of 1.1 for both the 2 and 4 h annealing steps at 700 °C. The barrier height increases from a value of 0.71 eV for the as-deposited sample

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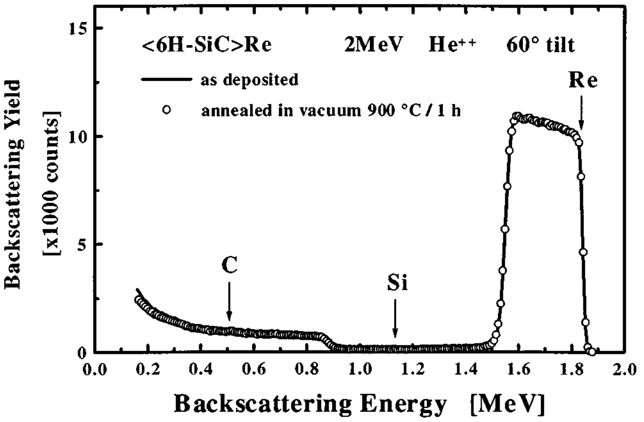

Fig. 1. MeV 4He^{++} backscattering spectra of a 100-nm thick Re film on 6H–SiC substrate before (solid curve) and after (open circles) annealing in vacuum at 900 °C for 1 h. The arrows mark the surface energy of the involved elements. (The angle of the incident beam against the sample normal is 60 °; the scattering angle of the detected particles is 165 °.)

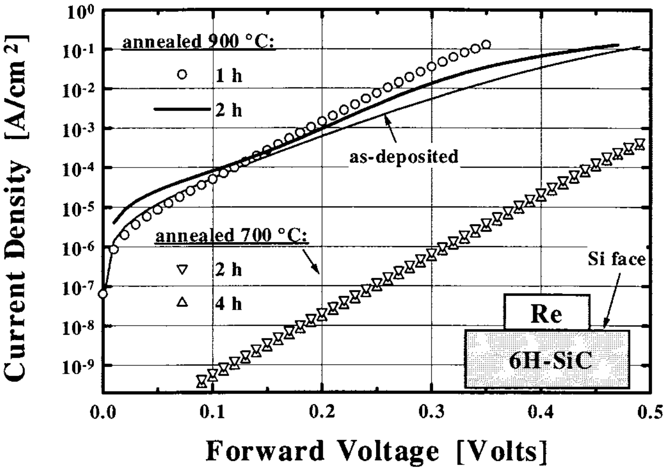

Fig. 2. A semilogarithmic *I–V* plot of a circular Re contact on the Si face of a 6H–SiC substrate before and after annealing in vacuum for 2 and 4 h at 700 °C and for 1 and 2 h at 900 °C.

to a value of 1.04 eV after the 700 °C annealing. A comparable behavior was reported for sputter-deposited TiN [6] and for W–Si–N and Ta–Si–N [7] Schottky diodes on n-type silicon. In both cases, an increase in barrier height is observed after annealing, and explained by annealing-out of donorlike traps formed by sputter-induced damage. Itoh *et al.* have shown that irradiation damage in SiC is completely annealed out when heat-treated in the temperature range between 600 and 800 °C [8]. In our case, this mechanism is further supported by improvement of the ideality factor upon annealing. Interface states are known to affect both the height of the Schottky barrier and the ideality factor of the diode [9], [10]. The changes in both parameters of different diodes were very small, suggesting rather a laterally uniform process, in support of the proposed mechanism.

Further annealing at 900 °C for 1 h alters the *I–V* parameters. The Schottky barrier height drops from 1.04 eV to 0.76 eV and the ideality factor rises from 1.1 to 1.25. The same results are obtained for a sample directly annealed at 900 °C (not shown). An additional 1 h annealing at 900 °C further increases the ideality factor from 1.25 to 1.36 and introduces a leakage current component, which is commonly attributed to recombination in the depletion region. Local atomic displacements that may take place upon annealing at 900 °C [11], [12] can significantly alter the electronic transport across the interface while remaining undetected by cross-sectional transmission electron microscopy even after vacuum annealing at 1100 °C for 30 min. [2] Similar observations were attributed by Tung to an inhomogeneity of the Schottky barrier height [13]. Our measurements, however, cannot provide this type of microscopic information.

Most papers reporting electrical characterization of annealed Schottky contacts to SiC have been carried out after rapid thermal annealing or at temperatures below 500 °C [14]–[18]. Kennou *et al.* studied the formation of Re contacts to 6H–SiC. They reported a barrier height of 0.7 ± 0.2 eV, which, despite initial chemical changes observed by XPS, appeared to be unaffected by successive 2 min heat treatments of up to 800 °C [19]. However, 2 min heat treatments are probably not sufficient to determine the device thermal stability. Hence, the finding of Kennou *et al.* does not rule out that longer heat treatment would lead to a change of the Schottky barrier. Moreover, they observed minor chemical changes evidenced in the form of the of the C(1s) and Si(2p) XPS peaks at the interface. This observation is in line with the lowering of the Re/SiC Schottky barrier observed in this work after annealing at 900 °C. Bhatnagar *et al.*reported on annealing of Pt and Ti contacts to 6H–SiC. [20] They observed an increase of both the barrier height and the ideality factor of the Pt contacts and no change in the Ti contacts after 30 min annealing at 600 °C. Lundberg *et al.*observed an increase of the ⟨6H–SiC⟩\Co Schottky barrier height from 0.79 to 1.30 eV after 1 h anneals at temperatures ranging from 300 to 800 °C and a decrease to 0.6 eV after further annealing at 900 °C [21]. The corresponding ideality factors were observed to decrease up to 600 °C, and to increase above it, in correlation with the onset of Co reaction with SiC. Similar results were reported by Porter *et al.* [22]. Contacts of Ti to 6H–SiC have also been studied by the same authors but did not show substantial changes in the Schottky barrier properties upon annealing for various periods up to 60 min at 700 °C in spite of the observed chemical reaction [23]. Pt was shown to react with the Si-face of 3C-, [24] 6H-, [25] and 4H–SiC [26] between 450 and 600 °C. Hence, Ti, Co, and Pt show initial stages of reaction with SiC after annealing at 700 °C and thus have unstable electrical characteristics. The reported heat treatments are therefore insufficient to establish thermodynamic equilibrium. Consequently, the electrical characteristics of these contacts are prone to change upon prolonged use at high temperatures. This limitation does not apply to contacts of Re, which is the only metal known to be thermodynamically stable with SiC, and, as shown herein, also provides a stable Schottky barrier at 700 °C.

IV. CONCLUSION

Rhenium is thermodynamically stable in contact with SiC. The measurements done at different stages of heat-treated 6H–SiC/Re couples show that this chemical stability is advantageous for the thermal stability of the resulting *I–V* characteristics, which is stable for hours of annealing at temperatures as high as 700 °C. Yet, the chemical stability of the contacting layer by itself is insufficient to prevent changes in the electrical characteristics upon initial annealing. Minor thermally induced interfacial modifications, too small to be detected even by advanced structural analysis, evidently alter the electronic transport across the SiC/metal interface in major ways. Some of these changes may be attributed to the removal of sputtering-induced defects that act as electron traps and are introduced at the SiC near-surface during film deposition. Thermal annealing of these traps raises the barrier height, as is also observed in the present case. Other changes, such as diffusion of impurities or defects may account for the observed deterioration of the contact at 900 °C.

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REFERENCES

[1] A. W. Searcy and L. N. Finnie, “Stability of solid phases and the ternary systems of Si and C with Re and the six Pt metals,” *J. Amer. Ceram. Soc.*, vol. 45, pp. 268–273, Jun. 1962.
[2] J. S. Chen *et al.*, “Stability of Rhenium thin films on single crystal (001) beta- SiC,” *J. Appl. Phys.*, vol. 75, pp. 897–901, Jan. 1994.
[3] C. D. Lien, F.C. T. So, and M.-A. Nicolet, “An improved forward I–V method for nonideal Schottky diodes with high series resistance,” *IEEE Trans. Electron Devices*, vol. ED-31, pp. 1502–1503, Oct. 1984.
[4] S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. New York, 1981, p. 280.
[5] J. R. Waldrop, R. W. Grant, Y. C. Wang, and R. F. Davis, “Metal Schottky barrier contacts to alpha 6H–SiC,” *J. Appl. Phys.*, vol. 72, pp. 4757–4760, Nov. 1992.
[6] M. Finetti, “Schottky barrier height of sputtered TiN contacts on silicon,” *Solid-State Electron.*, vol. 27, pp. 617–623, July 1984.
[7] L. E. Halperin, M. Bartur, E. Kolawa, and M.-A. Nicolet, “Silicon schottky barriers and p-n junctions with highly stable aluminum contact metallization,” *IEEE Electron Device Lett.*, vol. 12, pp. 309–311, June 1991.
[8] H. Itoh, N. Hayakawa, I. Nashiyama, and E. Sakuma, “Electron spin resonance in electron-irradiated 3C-SiC,” *J. Appl. Phys.*, vol. 66, pp. 4529–4531, Nov. 1989.
[9] R. F. Broom, “Doping dependence of the barrier height of palladium-silicide Schottky diodes,” *Solid-State Electron.*, vol. 14, pp. 1087–1092, Nov. 1971.
[10] G. H. Parker, T. C. McGill, and C. A. Mead, “Electric field dependence of GaAs Schottky barrier,” *Solid-State Electron.*, vol. 11, pp. 201–204, Mar. 1968.
[11] R. Kaplan, “Surface structure and composition of beta– and 6H–SiC,” *Surf. Sci.*, vol. 215, pp. 111–134, May 1989.
[12] L. M. Porter and R. F. Davis, “A critical review of ohmic and rectifying contacts for silicon carbide,” *Mater. Sci. Eng.*, vol. B34, no. 2–3, pp. 83–105, Nov. 1995.
[13] R. T. Tung, “Electron transport in metal-semiconductor interfaces: General theory,” *Phys. Rev. B*, vol. 45, pp. 13 509–13 523, Jun. 1992.
[14] K. Yasuda, T. Hayakawa, and M. Saji, “Annealing effects of Al/n-type 6H–SiC rectifying contacts,” *IEEE Trans. Electron Devices*, vol. ED-34, pp. 2002–2008, Sept. 1987.
[15] M. Bhatnagar, P. K. McLarty, and B. J. Baliga, “Silicon–carbide high-voltage (400 V) Schottky barrier diodes,” *IEEE Electron Device Lett.*, vol. 13, pp. 501–503, Oct. 1992.
[16] J. R. Waldrop and R. W. Grant, “Schottky barrier height and interface chemistry of annealed metal contacts to alpha 6H–SiC: Crystal face dependence,” *Appl. Phys. Lett.*, vol. 62, pp. 2685–2687, May 1993.
[17] P. Shenoy *et al.*, “Vertical schottky barrier diodes on 3C–SiC grown on Si,” in *IEDM Tech. Dig.*, 1994 , pp. 411–414.
[18] R. Raghunathan, D. Alok, and B. J. Baliga, “High voltage 4H–SiC Schottky barrier diodes,” *IEEE Electron Device Lett.*, vol. 16, pp. 226–227, June 1995.
[19] S. Kennou, A. Siokou, I. Dontas, and S. Ladas, “An interface study of vapor-deposited rhenium with two (0001) polar faces of single crystal 6H–SiC,” *Diamond Rel. Mater.*, vol. 6, pp. 1424–1427, Aug. 1997.
[20] M. Bhatnagar *et al.*, “Comparison of Ti and Pt silicon carbide Schottky rectifiers,” in *IEDM Tech. Dig.*, 1992, pp. 789–792.
[21] N. Lundberg and M. Ostling, “Formation and characterization of cobalt 6H–SiC Schottky contacts,” *Appl. Phys. Lett.*, vol. 63, pp. 3069–3071, Nov. 1993.
[22] L. M. Porter *et al.*, “Chemistry, microstructure, and electrical properties at interfaces between thin films of cobalt and alpha (6H) silicon carbide (0001),” *J. Mater. Res.*, vol. 10, pp. 26–33, Jan. 1995.
[23] L. M. Porter *et al.*, “Chemistry, microstructure, and electrical properties at interfaces between thin films of titanium and alpha (6H) silicon carbide (0001),” *J. Mater. Res.*, vol. 10, pp. 668–679, Mar. 1995.
[24] J. S. Chen *et al.*, “Solid-state reaction of Pt thin film with single-crystal (001) beta–SiC,” *J. Mater. Res.*, vol. 9, pp. 648–657, Mar. 1994.
[25] S. M. Gasser, I. Shalish, E. Kolawa, and M.-A. Nicolet, “Differences between solid state reaction of Pt thin film deposited on C- and Si-face of 6H–SiC,” in *Proc. 3rd Int. Conf. High-Temperature Electronics*, Albuquerque, NM, 1996.
[26] I. Shalish, C. E. M. de Oliveira, Y. Shapira, and M. Eizenberg, “Thermal stability of Pt Schottky contacts to 4H–SiC”, submitted for publication.