High-temperature characteristics of diamond Schottky diodes using various Schottky metals

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Abstract
High-temperature characteristics and stability of diamond Schottky diodes using various Schottky metals were examined. Cu and Ag/diamond Schottky diodes showed clear rectification up to ~750°C, indicating the diodes can work even at ~750°C. High rectification properties of these diodes at higher temperature are considered to be due to higher Schottky barrier heights (~1.7 eV). Cu Schottky diodes have higher stability up to 700°C probably because of smaller interfacial reactions and/or interdiffusion between Cu Schottky electrodes and diamond.

1. Introduction
Diamond is a promising semiconductor for high-power and high-frequency devices due to its excellent physical properties. These properties are advantageous for producing high-frequency and high-power devices [1]. Because of its wide band gap (~5.5 eV) and high chemical stability, diamond is also promising for high-temperature applications, such as devices used close to automobile engines. The intrinsic carrier concentration for diamond is estimated to be ~10^{10} cm^{-3} at 1000°C based on its band gap. This is comparable to that for Si at room temperature, suggesting that diamond devices can operate above 1000°C. Although there have been several studies on the high-temperature characteristics and thermal stability of diamond Schottky diodes, most were performed at temperatures below ~500°C. At temperatures of several hundred degree C, one important application is in devices used in automobiles such as power devices for inverters, and SiC is a strong competitor to diamond in this temperature range. However, there have only been few reports on the characteristics of diamond Schottky diodes at temperatures above 500°C, where diamond can offer advantages over other semiconductors because of factors such as its very high thermal conductivity, small leakage current, and activation of deep acceptor (boron). Therefore, it is important to fabricate diamond devices that exhibit high thermal stability above 500°C and clarify high-temperature deterioration mechanisms.

In this study, Schottky diodes working well above 500°C were fabricated and their high-temperature characteristics were investigated up to ~800°C.

2. Experimental
B-doped homoepitaxial diamond films were grown on commercial diamond (100) Ib substrates by microwave plasma chemical vapor deposition (CVD) [2]. Schottky diodes using various metals (Cu, Ag, Ni) were fabricated on the B-doped diamond films, whose conductivity was originated from unintentionally doped B during the CVD growth. Typical acceptor concentration and room temperature mobility was ~10^{17} cm^{-3} and ~1000 cm^{2}/Vs, respectively. The widely used UV/ozone treatment was applied to convert the hydrogen-terminated surfaces of the as-grown B-doped diamond films to oxygen-terminated surfaces before depositing Schottky and ohmic electrodes. Current-voltage (I-V) characteristics of the Schottky diodes were measured in vacuum up to ~800°C.

3. Results and Discussion
Figure 1 shows current voltage characteristics of Cu/diamond Schottky diodes measured from room temperature (R. T. : ~25°C) to 800°C. A high rectification ratio of ~10^5 was observed at R.T. The reverse leakage current was lower than the detection limit of our instruments at temperatures below 100°C, indicating that the rectification ratio was more than 10^5. Forward current systematically increased as temperature increased by activation of B acceptors. The reverse leakage current also increased as...
temperature increased, however the rectification ratio remained $\sim 10^3$ below 600°C. And, rectification ratio of more than 10 was obtained even at 700°C, indicating Cu/diamond Schottky diodes can work at $\sim 700°C$. On the other hand, Ag Schottky diodes showed similar temperature dependence of I-V curves with that of Cu Schottky diodes and the rectification ratio kept $\sim 10$ even at $\sim 750°C$ [3]. In the case of Ni Schottky diodes, the reverse current systematically increased as temperature increased and no clear rectification was observed above $\sim 600°C$.

By analysis of the I-V characteristics of the diodes by the thermionic emission (TE) model, the Schottky barrier height ($\phi_B$) was estimated to be $\sim 1.6$ eV, $\sim 1.7$ eV and $\sim 0.6$ eV for Cu, Ag and Ni Schottky diodes, respectively. Maximum working temperature of the Schottky diodes was increased as $\phi_B$ increased. We consider high rectification ratio of the Cu and Ag diodes at higher temperature is due to higher $\phi_B$, and it is a prerequisite for fabricating diamond devices working at higher temperature.

To check high temperature stability of the Cu and Ag Schottky diodes, I-V characteristics at room temperature were measured after high temperature annealing of the diodes at 600–800°C for 30 min. In the case of Cu Schottky diodes, the I-V characteristics at R. T. were almost same, that is, no change in reverse leakage current after high temperature annealing below 700°C (Fig. 2). We consider slight change of the forward I-V characteristics after high temperature annealing above 600°C is due to improvement of contact resistance of ohmic electrodes. These results indicate that the Cu Schottky diodes are stable up to $\sim 700°C$. On the other hand, in the case of Ag Schottky diodes, the reverse leakage current increased as annealing temperature ($T_a$) increased (Fig. 3). The reverse leakage current of Ag diodes became larger as $T_a$ increased. This means that the Ag diodes have problems in longer time stability though working temperature was higher than that of Cu and Ni diodes. The reason for the deterioration is not currently clear, but we consider it to be related to interfacial reactions and/or interdiffusion between the diamond film and the Ag Schottky electrodes. Teraji et al. suggested that deterioration of Au/diamond Schottky diodes occurs at high temperatures due to breakdown of the oxygen termination of the diamond surface beneath the Au electrode, which occurs at temperatures above $\sim 500°C$ [4]. In the case of Ag Schottky diodes used in the present study, it is considered that this may have led to a reaction between highly reactive electrode metals such as Ag and carbon dangling bonds on the diamond surface.

4. Conclusions
High-temperature characteristics and stability of diamond Schottky diodes using various Schottky metals (Cu, Ag, Ni) were examined. Cu Schottky diodes have high stability even at 700°C. We consider Cu/diamond Schottky diodes are promising for using in high temperature devices working well above 500°C.

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