THERMISTER MADE OF DIAMOND THIN FILM

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It is widely held that diamond can be applied to refractory semiconductors due to its wide band gap and chemical stability. The authors have for the first time fabricated a thermistor made of a polycrystal diamond thin film and characterized its properties. Thermisters made of boron-doped diamond films are considered to be useful under a wide temperature range from R.T. to 600°C, having a resistance of $10^4$~$10^5$ Ω at R.T. and $10^7$~$10^9$ Ω at 600°C and a thermistor constant of 5800. Ti electrodes were used for good ohmic contacts, and Si$_3$N$_4$ or AlN were suitable as substrates.

1. Introduction

The CVD method of producing a diamond film on a substrate from the gas phase reaction has been developed recently, and has been researched and improved remarkably until today. Diamond is considered useful in various applications capitalizing on its super hardness, extremely high thermal conductivity, excellent optical transmittance and/or chemical stability.

The application of diamond in an electrical capacity as a semiconductor is an attractive subject. In comparison with other semiconductors, diamond has a wide band gap (5.5 eV), a high thermal conductivity (20 w/cm·K), a small relative dielectric constant (5.7), high hole-and-electron mobilities and a high breakdown voltage, so it is expected that we will be able to make new devices from diamond that can operate at high temperatures, high power and high speeds. Diamond is chemically stable up to 800°C in air, and doesn’t have an intrinsic region as a semiconductor, theoretically. A refractory semiconductor device which can operate at high temperatures of several hundred degrees °C can be fabricated using diamond.

Diamond is an insulator in itself, but doped with boron, it turns into a P-type semiconductor and becomes conductive. The authors have already succeeded in preparing an epitaxial diamond thin film and doping some elements into it, and have investigated especially a boron-doped P-type diamond film, succeeding in fabricating a Schottky diode with it.

Figure 1 shows the temperature dependence of carrier concentration, hole mobility and resistivity of a boron-doped epitaxial diamond film. As the temperature increases from −50°C to 600°C, the carrier concentration increases from $10^{12}$ to $10^{18}$ (1/cm$^3$) according to the activation energy of 0.38 eV, which is considered to be an acceptor level and the same value as that of a IIb crystal diamond.

![Fig. 1. Temperature dependence of carrier concentration, hole mobility and resistivity of boron-doped epitaxial diamond film.](image_url)

The hole mobility decreases due to the ionized impurity scattering system as the temperature rises above 0°C. Consequently, the resistivity decreases from $10^4$ to $10^{-1}$ Ω-cm as the temperature increases. This property suggests that diamond can be applied to a thermistor which operates in a wide temperature range.

Thermisters are widely used for sensors and temperature compensating devices of electronic circuits. Most of these are used at temperatures from R.T. to 400°C. A thermistor made of semiconductor diamond will operate in temperatures from R.T. to 500°C or more, and can therefore be used in severe conditions such as in controlling an engine, a heater, or an atomic pile.

Thermisters made of single crystal diamond have been reported before, but they have not been widely used due to their price and/or difficulty in manufacturing. The authors have fabricated thermisters made of polycrystal diamond films for the first time and characterized their properties.

2. Fabrication of diamond thermistor

The authors have fabricated a diamond thermistor as shown schematically in Fig. 2; its photograph is shown in Fig. 3.

The fabrication process was as follows; boron-doped or non-doped polycrystal diamond films were deposited on Si$_3$N$_4$ or AlN ceramic substrates. Insulators were chosen as the substrates because there are no worries about any remaining pin holes in the diamond film that would cause a short circuit. Among insulators Si$_3$N$_4$ and AlN are suitable substrate materials because they are chemically stable at high temperatures and a diamond film can easily be deposited on them. They were used after their surfaces were scratched with diamond powder to increase the generation of diamond nuclei. The size of the substrates was $1.5 \times 3.8 \times 0.7$ mm.

The microwave plasma CVD method was used to deposit the diamond film. The material gases used were H$_2$, CH$_4$ and B$_2$H$_6$ as the dopant boron gas. The ratio of CH$_4$/H$_2$ was 1/200 and B$_2$H$_6$/CH$_4$ was changed from 0 to 2000 ppm. The power of the microwave at 2.45 GHz was 400 W, and the reaction pressure was 40 Torr. The thickness of the deposited diamond film was 1~3 μm. An SEM image of the surface morphology of the diamond film is shown in Fig. 4. A mass of diamond grains smaller than 1 μm in diameter was observed on the

![Fig. 4. SEM image of surface morphology of diamond film on Si$_3$N$_4$.](image-url)
whole surface of the substrate. The grains had good diamond structures exhibiting sharp edges on their surfaces. No differences were observed between the diamond films on Si$_3$N$_4$ and on AlN.

Ti films were evaporated by E.B. on the diamond film as ohmic electrodes, and then Mo films covering the Ti films and Au films on the top were evaporated in order to protect the Ti films from oxygenation. Mo films were inserted to prevent the Ti films and Au films from alloying at high temperatures.

A SiO$_2$ film or an Al$_2$O$_3$ film was deposited on the diamond film for the purpose of passivation.

Ni wires were used as leads which were fixed to the electrodes with heat-resistant silver paste.

3. Characterization of diamond thermister

3.1 Temperature dependence of resistance

These thermisters were measured for their electrical resistance in a temperature range from R.T. to 600°C in air. The resistance was measured by a bias voltage of $-10^{-10}$ V. The current-voltage characteristic was ohmic at any temperature.

Figure 5 shows the temperature dependencies of the resistance of the diamond thermisters using Si$_3$N$_4$ substrates. In the thermisters made of boron-doped diamond films, the resistance got smaller as the concentration of doped boron increased. The resistances were $10^5$ to $10^9$ Ω at R.T., which corresponds to resistivities of $10^0$ to $10^5$ Ω cm. As the temperature increased, the resistances decreased constantly, and at 600°C they were $10^2$ to $10^5$ Ω, which corresponds to resistivities of $10^3$ to $10^7$ Ω cm. Above 600°C the resistance was not stable. The activation energy calculated from the Arrhenius plot of the resistance got smaller as the concentration of doped boron increased, and the resistance got smaller. When the concentration of doped boron (B$_2$H$_6$/CH$_4$) was 20 ppm, the activation energy $E_a$ was 0.50 eV, which gives a thermister constant of 5800; when the concentration of doped boron was 200 ppm the activation energy was 0.24 eV, which gives a thermister constant of 2800.

These characteristics are similar to those of boron-doped epitaxial diamond films and b diamond crystals, even though there should be some influence of the grain boundaries of the polycrystal diamond films and some differences in the crystallinity of the diamonds. When the concentration of doped boron was 2000 ppm the resistance was almost independent of the temperature, which is considered to be due to degeneration of the acceptor level. This diamond film had poorer crystallinity judging from the observation of the surface morphology by SEM, and its resistance was not stable at high temperatures.

As for the thermister made of a non-doped diamond film, the resistance was more than $10^{13}$ Ω at R.T. and decreased to $10^5$ Ω as the temperature increased to 600°C. The activation energy was 0.60 eV and the thermister constant was 7000.

The characteristics of the thermisters using AlN substrates were much the same as all those using Si$_3$N$_4$ substrates.

It is thought that the characteristics can be controlled by changing the deposition conditions of the diamond film and the design of the substrate, diamond film and electrodes. These changes can be controlled relatively easily compared to when using a crystal diamond, and this is a big asset of using diamond thin film.

Fig. 5. Temperature dependence of resistance of diamond thermister.
3.2 Endurance test
The durability of the thermistor was tested. This is an important point in putting a thermistor to practical use. Although diamond is considered to be chemically stable in temperatures up to 800°C in air, the resistance of these diamond thermisters was not perfectly stable. For the best sample, the resistance rose by 5% after being kept at 500°C for 100 hours. Above 600°C the change of the resistance grew considerably larger, and even the passivation film would crack and peel away from the diamond film. The change was larger for samples without passivation.

When a thermistor consisted of a less-crystalline diamond film deposited under the condition of CH₄/H₂ = 3%, the durability got worse. The resistivity rose by five orders after being kept at 500°C in air for 10 hours. Figures 6(a), (b), (c) and (d) are SEM images showing the changes of surface morphologies of diamond films without passivations after they were kept at 500°C. It is observed that every diamond grain is etched from its edges after the heatings in air, and the degree of etching is much greater for the less crystalline diamond film.

The durability will be improved by optimizing the condition of the passivation film and the diamond film that is now being experimented with.

4. Conclusion
The authors have fabricated thermisters made of polycrystal diamond films for the first time. The resistances of the thermisters made of boron-doped diamond films were $10^4 \sim 10^9 \, \Omega$ at R.T. and $10^2 \sim 10^5 \, \Omega$ at 600°C, and their thermister constants were 5800. These thermisters are considered to be useful in a wide temperature range. The resistance of the thermister made of non-doped diamond film was more than $10^{13} \, \Omega$ at R.T. and $10^6 \, \Omega$ at 600°C, and its thermister constant was

![SEM images of surface morphology of diamond films deposited under different conditions and heated in air with no passivation. (a) Deposited under conditions of CH₄/H₂ = 0.5%, as grown. (b) Deposited under conditions of CH₄/H₂ = 3%, as grown. (c) After 500°C for 100 hours in air (a). (d) After 500°C for 10 hours in air (b).](image-url)
7000. This thermister may be useful at high temperatures.

Durability of thermisters is closely related to passivation and crystallinity of the diamond films used. Better passivation and optimization of the diamond film will improve durability.

REFERENCES


