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Ohmic contacts have been successfully made to naturally doped semiconducting diamond using evaporated thin films of molybdenum, molybdenum/gold, and molybdenum/nickel/gold. The metal contacts form a tenacious bond with the diamond substrate after annealing. The time and the temperature of annealing also affects the type and the degree of conduction of the contacts.

Characterization of the interface of the metal contacts to diamond using AES, SIMS, RBS, XRD, SEM, and metallography clearly indicates that metal–carbide–precipitates nucleate and grow at the diamond/metal interface during annealing. It is concluded that the size and the areal density of the carbide precipitates at the interface are the principal factors that control the adhesion, and the mode and the degree of conductivity of the metal contacts.

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METALLIZATION OF SEMICONDUCTING DIAMOND: Mo, Mo/Au and Mo/Ni/Au.

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INTRODUCTION

The goal of this research is to develop a technology to produce reliable, reproducible, low resistance ohmic contacts to thin films of epitaxial monocrystalline diamond. Implicit in this goal is the requirement that the techniques be compatible, as far as possible, with conventional manufacturing practice in the microelectronic industry. Further, it is assumed that the ohmic contacts to diamond are intended for diamond devices operating at temperatures exceeding 400° Celsius and in environments that are, very likely, corrosive and/or contain high levels of radiation.

Inasmuch as, epitaxially grown monocrystalline semiconducting films of diamond were unavailable at the inception of this research effort, naturally boron-doped semiconducting diamond samples were used in this study. The

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rationale being that the processes developed for producing ohmic contacts to natural diamond could be adapted to synthetically grown diamond films in a shorter time period than delaying the research until such time as synthetically grown films would be availabe for study.

Over the years, a number of investigators [1-3] have used a variety of techniques for making ohmic contacts to diamond. These techniques were found to be unsuitable for the present purposes; either because they are labor intensive, lack reproducibility, or can not withstand the rigors of the intended operating conditions cited above. More recently, an approach for making ohmic contacts that relies on "ion mixing" has been suggested [4]. While this approach is not beset with the shortcomings cited above, it does raise concern regarding the effect of the damage, introduced during implantation, on the physical and electrical properties of semiconducting diamond.

At the outset, it was postulated that both the adherence and the conductivity of the contacts were dependent on the formation of a primary chemical bond between the contacting material and the diamond. Consequently, the choice of the contacting material was limited to carbide forming metals. The requirement that the diamond devices, for which the ohmic contacts were being developed, were to be used at elevated temperatures further limited the choice of the contacting material to refractory or quasi-refractory carbide forming metals. It was recognized that these metals were susceptible to corrosion, consequently, in most instances, a layer of a noble metal such as gold was deposited on the "reactive" metal.

In a series of studies, a number of metal films including molybdenum, molybdenum/gold, molybdenum/nickel/gold, nickel, tantalum/gold, titanium/gold, and titanium platinum were investigated and the results reported elsewhere [5-7]. In this report, recent results that have been obtained with molybdenum, molybdenum/gold, and molybdenum/nickel/gold ohmic contacts to naturally doped diamond substrates will be discussed.

EXPERIMENTAL PROCEDURES

The diamond samples that were used in this study consisted of naturally boron-doped p-type semiconducting diamond (class IIb) with the dimensions of 5 x 5 x 1/4 mm or 4 x 4 x 1/4 mm. The boron concentrations were in low to mid 10E16 and carrier concentrations in high 10E13 to low 10E14.

Briefly, the experimental procedures consisted of cleaning the diamond substrates using decontam, Q-water, and ethanol, sequentially. The samples were then baked at 120° Celsius for ~ to 30 minutes and loaded into an ion-pumped ultra-high vacuum system. The diamond samples were metallized using either an electron beam evaporation source (for metals having melting

temperatures exceeding 1500° Celsius) or by using a resistively heated evaporation source (for metals having melting temperatures below 1500° Celsius). The thickness of the deposited "carbide forming" metals had a range of 5 to 25 nm, whereas, the noble metal films had a range of 150 to 500 nm in thickness. Multicomponent films were usually deposited, in situ, sequentially to produce an abrupt interface and to minimize alloying, although on several occasions, graded interfaces were produced by simultaneous evaporation of two metals to determine if this factor affected the adhesion of the films.

Following deposition, the metallized samples were baked at 120° Celsius for approximately 20 to 30 minutes and then annealed, usually, in a tube furnace in an atmosphere of purified hydrogen gas. Some of the samples were also annealed in a rapid thermal annealing (RTA) furnace to determine the most suitable annealing regime.

Current-voltage characteristics were measured, usually, on a curve tracer. Materials characterization consisted of Auger electron spectroscopy (AES), Rutherford backscattering spectroscopy (RBS), secondary ion mass spectroscopy (SIMS), galvanomagnetic measurements, scanning electron microscopy (SEM), x-ray diffraction (XRD), and metallography.

The specific procedures used in producing ohmic contacts to natural diamond substrates using molybdenum, molybdenum/gold, and molybdenum/nickel/gold films were: a) Deposited molybdenum films with thickness of 5 to 25 nm using an electron beam vaporization source. b) Deposited nickel films with thickness of 15 to 25 nm. c) Deposited gold films with thickness of 150 to 250 nm using resistively heated vaporization source. d) Baked samples at 120° Celsius for 20 minutes. e) Annealed samples at 950 ± 10° Celsius for various times from 30 seconds to 16 minutes. f) Measured the I-V response as a function of annealing time. g) Characterized the diamond/metal interface.

RESULTS AND DISCUSSION

As has been reported earlier [5-7], the electrical response of the annealed samples exhibited a sharp decrease in resistance (exceeding ten orders of magnitude) relative to the as-received and the metallized samples prior to annealing. Further, the I-V characteristics of the annealed samples exhibited a linear relationship between the applied potential and the current flow over a wide range of applied potentials. Moreover, the resistance of the contacts was strongly dependent on the time and the temperature of annealing. The resistance of the contacts decreased sharply with annealing time to a minimum value at 6 to 8 minutes and increased slightly as the time increased beyond 8 to 10 minutes. The minimum resistance attained was approximately 500 ohms for contact pads with separation distance of 5 μm.

SIMS and RBS examination of the metallized samples indicated that molybdenum had penetrated into the diamond substrate during annealing. Metallographic and SEM examination of the metallized and annealed samples revealed the presence of precipitates at the diamond/metal interface. AES analysis indicated that the "shoulder" preceding the main carbon KLL transition line (nominally at 270 eV) changed its shape from that associated with adsorbed carbon to that associated with carbon compounds to that associated with diamond as depth profiling was effected from the air/metal interface through the metal/diamond interface. XRD studies of the annealed molybdenum, and molybdenum/gold contacts established that the precipitate at the diamond/metal interface is a carbide of molybdenum with a high degree of preferred orientation as evidenced by the presence of a single dominant peak at $2\theta=37.8°$. Due to the extreme thinness of the films, it was not possible to differentiate between Mo_2C and $Mo_{24}C_{58}$.

The formation of the molybdenum carbide precipitates at the metal/diamond interface, as shown in Figure 1, is thought to be responsible for the dramatic change in the electrical response of, and the tenacious adherence of the annealed metal contacts to diamond. The tenacity of the contacts is demonstrated by the ability to attach adherent gold wires to the metallized diamond samples by an ultrasonic wire bonding process, as shown in Figure 2. The 5 x 5 x 1/4 mm diamond sample was lifted by the gold wire and the bonds supported its total weight.

Figure 1. SEM micrograph of molybdenum/gold contact to diamond after annealing and etching to remove the excess metal.

Figure 2. A scanning electron micrograph of a ball and a wedge bond to a molybdenum/gold contact to a diamond substrate.

CONCLUSIONS

During annealing of molybdenum, and molybdenum/gold contacts to naturally doped semiconducting diamond, a molybdenum carbide precipitate nucleates and grows at the diamond/metal interface. The electrical response of the contacts is a function of size and areal density of the precipitates. The electrical resistance of the contacts reaches a minimum value prior to the formation of a monolithic carbide phase at the interface.

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