SECTION C, PHYSICAL SCIENCES

Electrical Contacts to Semiconducting Diamonds[1]

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INTRODUCTION

The successful use of insulators and semiconductors in electrical devices such as rectifiers, transistors, and photo-detectors has depended upon the ability to produce low-noise electrical contacts having desirable electrical and mechanical characteristics. The transistor itself was invented as a result of investigations of the nature of a metal-to-semiconductor contact. The studies reported herein are the outgrowth of studies of the electrical and optical properties of semiconducting diamonds (Bell and Leivo, 1958). Our recent studies of magnetoresistance of semiconducting diamonds in high-pulsed magnetic fields (500 kG) showed the need to produce low-noise ohmic contacts having high mechanical strength. Without strong mechanical contacts the electrical leads would be forced from the diamond because of the high magnetic field. Also, our studies of photoconductivity at liquid helium temperatures required electrical contacts which were not seriously affected by the stresses produced by temperature changes.

The metal contacts considered herein are silver paint, titanium hydride, low-melting-point solders, probe contacts using thermo-compression, and evaporated contacts. The relative merits of the contacts will be discussed briefly in a later section; however, the titanium hydride method makes the best electrical contact, and it has the greatest mechanical stability and strength.

COMMENTS ON THE NATURE OF CONTACTS TO DIAMONDS

The simple method of applying silver paint contacts to semiconducting diamonds has proven to be only partially successful so far as good electrical contact is concerned. Although a non-ohmic contact is desired in cases such as the photovoltaic effect, it is usually desirable to have a low-noise ohmic contact which is mechanically stable. In Table I are listed several types of contacts that have been found useful by other investigators.

The technique of bonding diamond to metals using titanium hydride and silver solder was used by Pearsall and Zingeser (1949) which is the same as Bondley's (1947) method that was used on ceramics. Further use of this method was achieved by Hall (1954) when he mounted diamonds on tools using TiH_2 and silver-copper eutectic solder. Another technique which is similar to the TiH_2 method makes use of Ti - Ag - Cu eutectic wire (Rodgers and Raal, 1960); however, it should be noted that a temperature of 1200 C was used. Details of the TiH_2 method will be given later.

It appears that the evaporation of contacts onto the diamond surface has not proven to be very successful, from the small number of investigators that have reported on such contacts. Our experience is that evaporated contacts of various metals (Al, Ag, Cu, Au, Pt) are mechanically stable but noisier than silver paint contacts. Perhaps the answer to this problem is associated with the wetting of the diamond surface as it has been shown that these metals do not wet the surface readily

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TABLE I. METAL-DIAMOND CONTACTS

Type of Electrodes	Investigation	Remarks
Evaporated aluminum	Effect of light on diamond counter[a]	
Titanium hydride + silver solder	Mounting of diamonds in tools[b]	Suggested use in electrical measurements
Indium and silver paint	Hall effect and rectification[c]	Neither contact was ohmic at all temperatures
Evaporated silver tungsten probe	Rectification and resistivity[d]	Probe contact resistance varied over diamond surface
Colloidal graphite in water with spring-loaded copper probes or plates	Hall effect and resistivity[e]	Graphite used on both faces and as spot contacts
Graphite block pressed on to diamond with chromel wire wedged under. Aluminum, copper, nickel, platinum, tungsten and graphite used as other probe materials	Electroluminescence[f]	Observed same color with all probe materials
Diamond pressed between copper rivets	Thermoelectric power of IIb diamonds[g]	Best contacts made along edges of diamond
Surface roughened with #600 Carborundum powder, contacts made with silver paint	Hall effect[h]	Contacts were ohmic and of very low resistance
Surface roughened with 8-12 mesh diamond powder, contacts made with silver paint	Resistivity changes[i]	Diamond and silver contacts were baked at 400 C for 20 min
Titanium-silver-copper eutectic wire with platinum leads	Thermistor action[j]	Heated diamond to 1200 C. Ohmic contact
Pressed silver-Aquadag contacts and graphite blocks	Resistivity of IIb diamonds[k]	Method produced stable and reproducible contacts

References pertinent to Table I—*a.* Kojima S. and S. Kono. 1952. J. Phys. Soc. Japan 7:84; *b.* Hall, H. T. 1954. Rev. Sci. Instr. 25:1035; *c.* Brophy, J. J. 1955. Phys. Rev. 99:1336; *d.* Dyer, H. B. and P. T. Wedepohl. 1956. Proc. Phys. Soc. (Lond.) B69:410; *e.* Wedepohl. 1957. Proc. Phys. Soc. (Lond.) B70:177; *f.* Wolfe, R. and J. Woods. 1957. Phys. Rev. 105:921; *g.* Goldsmid, H. J., C. C. Jenns and D. A. Wright. 1958. Proc. Phys. Soc. (Lond.) B73:393; *h.* Bate, R. T. and R. K. Willardson. 1959. Tech. Doc. AFOSR-TN 58-916, ASTIA-AD-204565, Tech. Note #2; *i.* Mutch, R. E. and F. A. Raal. 1959. Nature 184:1857; *j.* Rodgers, G. B. and F. A. Raal. 1960. Rev. Sci. Instr. 31:663; *k.* Johnson, A. D., J. R. Littler and J. P. Wielhouwer. 1962. AFCRL-62-561, ASTIA-AD-407912.

(Naidich and Kolesnichenko, 1964). This is illustrative of the fact that good mechanical bonds do not necessarily make good electrical contacts.

TECHNIQUES OF MAKING CONTACTS TO DIAMONDS

The success of applying any electrical contact to a nonmetallic substance depends in part on the cleaning of the surface before application. The following procedure was established to insure a clean diamond surface:

(1) Reflux for 24 hr in methyl alcohol or trichloroethylene.

(2) Treat in acid bath of warm nitric acid or aqua regia.

(3) Rinse with distilled water and methyl alcohol.

A relatively clean diamond surface was assumed when using the above procedure. If the diamond had been coated previously with metal or other contaminants, then special cleaning procedures may be necessary. Every-day cleaning of the diamonds for general use may simply consist of successive baths in an organic solvent, nitric acid, distilled water, and alcohol. After cleaning, the contacts are applied.

Silver paint (DuPont 4817) contacts were applied and allowed to age from 3 days to 2 weeks at room temperature. Contacts made with the paint were also cured at 90 C. The better silver paint contacts were those which were room-temperature-cured for two weeks. The noise associated with the silver paint contacts is very large and contains a constant noise level plus noise pulses. The noise is voltage-dependent, and there appears to be no correlation between the humidity and amplitude of the generated noise. Silver paint contacts are, as one would expect, mechanically unstable at low temperatures. No attempt was made to measure the noise spectrum. It should be noted that on cleaning silver paint from the diamond there is usually a resin film left that is acid-resistant. The film may be removed with a solvent such as butyl acetate.

When a metallic contact is made to diamond using titanium hydride it is necessary to heat the diamond to a temperature greater than 500 C in an inert atmosphere or in a vacuum. Care should be taken to keep the temperature below 1000 C because above this temperature the rate of change of diamond to graphite becomes excessive. A 325-mesh titanium hydride powder is applied to the diamond in the form of a colloidal suspension in amyl acetate which contains a small amount of Acryloid resin. The resin makes the powder adhere to the diamond surface. A special solder alloy is then sprinkled over the titanium hydride, and a small drop of amyl acetate is applied to make the solder adhere. Platinum lead wires can be attached before the titanium hydride is applied. The diamond with the powdered contact is then placed in a simple vacuum furnace. The furnace consists of a quartz tube of sufficient diameter to allow the diamond to be inserted and a nichrome heater ribbon wrapped around the tube to form a helix. The furnace with the prepared diamond is placed into a vacuum evaporation unit, and the entire system is evacuated to a pressure of 10^{-6} mm Hg. The temperature of the diamond is raised to 705 C for 10 min. The temperature can be monitored with an iron-constantan thermocouple. The decomposition of titanium hydride with the release of atomic hydrogen occurs rapidly near 700 C (Pearsall and Zingeser, 1949). It is the hydrogen that helps to clean the surface and aids in obtaining a better metal-diamond contact. This method of applying metallic contacts to semiconducting diamond has been used successfully in our laboratories for magnetoresistance studies at high-pulsed magnetic fields (Russell, 1965) and results in a mechanically and electrically stable contact. It should be noted that the contact surface of the diamond is etched and assumes a frosty appearance. However, the damage to the surface is slight, and the quality of the contacts allows measurements which could not have been obtained with other contacts since the noise is reduced by approximately a factor of 100 over that of silver paint contacts. The contact resistance was also reduced by two orders of magnitude, indicating that the formation of high-resistance layers at the metal-diamond interface did not affect the quality of the contact appreciably. One other item that is of interest is the removal of the contacts. The Ti-Incusil contact may be conveniently removed with a HNO_3 — HF acid mixture heated to approximately 90 C.

Probe contacts are useful in special measurements on semiconducting diamonds such as the Hall effect and magnetoresistance. This type of contact to diamond is difficult to obtain because of the desirability of a very small contact area. The thermo-compression technique used in making contacts to silicon and germanium offers several advantages in obtaining good probe contacts to diamond. In particular, equipment and special tools are readily available. The thermo-compression apparatus we constructed consists of the following components:

(1) Micromanipulator - the movements of the manipulator consist of micrometer motion in the *x-y* direction and a microscope motion in the *z* direction. A special mount holds the compression tool.

(2) Tempress thermo-compression tool with heating unit.

(3) Unitron microscope mounted on a special base so the contact operation may be observed.

(4) Heater platform to support the specimen and to maintain it at the desired temperature.

(5) Microflame torch.

The nail-head compression technique was utilized in the initial experiments using pure gold wire (0.002" dia.) for the contact metal. The contact was made to a type I diamond on the (111) face. The contact was not good, but the gold did adhere to the diamond surface. A slight roughening of the surface in the case of semiconducting diamonds should help in making this particular type of contact more stable mechanically. Also, the technique may be more successful if titanium wire is used since it is known to adhere to the diamond surface (Naidich and Kolesnichenko, 1964).

Low-melting solders such as indium have not produced as good a contact as those prepared by the TiH_2 method, but with the proper precautions it is possible that a usable contact may be obtained. Indium, lead and tin would not be expected to form a good contact to semiconducting diamond because these do not wet the surface. The addition of small amounts of Ti and Cr to nontransition metals increased their wetting of the diamond surface. Indium contacts were extremely noisy and mechanically unstable at low temperatures.

Even though evaporated contacts bond well to diamond, they have not proven to be as satisfactory as expected since they are noisier than silver paint. They are much more reliable, however, than paint contacts. The diamond is preheated in a vacuum to approximately 500 C before applying the contact. After heating, the contact is evaporated onto the diamond. The metals used included Al, Ag, Cu, Au, and Pt. Platinum gave the best contact and developed only a very small photovoltage at the metal-diamond contact at low temperatures.

SUMMARY

Titanium hydride has been used successfully in applying electrically and mechanically stable contacts to semiconducting diamonds. The TiH_2

contacts are being used in magnetoresistance measurements to provide relatively noise-free contacts. Probe contacts can be applied using thermocompression techniques, with some modifications, for measurements of the Hall effect and similar experiments where probe connections are required. Other contacts which have proven to be useful are silver paint, evaporated metals, and low-melting solders.

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