

Semiconducting Diamonds by Ion Bombardment

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Both natural and synthetic diamond crystals acquire altered surface layers as the result of ionic bombardment in a glow discharge at potentials of 1500–2800 V. The surface layers have a gray-brown color, and electron diffraction patterns of them indicate that they are somewhat amorphous. The surface layers are found to be electrical semiconductors. The kinds of gas ions used for bombardment apparently determine whether the conductivity is predominantly *n* type or *p* type. The activation energies for conduction range between 0.024 and 0.20 eV. The surface layers are partly destroyed by heating in air to about 400°C.

NATURALLY occurring semiconducting diamonds were described by Custers¹ in 1952. They are usually referred to as Type IIb diamonds, and their properties have been studied by several investigators.^{2,3,4} They are found to be *p* type semiconductors with activation energies for conduction in the range 0.29 to 0.38 eV and carrier mobilities of about 1000–1600 cm² sec⁻¹ V⁻¹. The resistivity varies between about 10² to 10¹⁰ Ω-cm and is frequently not constant throughout the same crystal.

Semiconducting diamonds may also be prepared in the laboratory by either of two high pressure, high temperature methods.⁵ In the growth method, boron, beryllium, or aluminum are added to the diamond synthesis mixture,⁶ typically graphite together with a suitable catalyst such as iron, nickel, etc. The diamonds which form out of the graphite are found to be *p* type semiconductors with resistivities in the range 10² to 10¹⁰ Ω-cm and activation energies for conduction in the range 0.17 to 0.32 eV.

In the diffusion method, natural or synthetic diamond crystals are made into *p*-type semiconductors by exposure to boron, boron carbide, etc., at temperatures above about 1600°C and diamond-stable pressures for times of minutes or hours. The conducting region of a crystal prepared in this way is usually a thin exterior layer which has a relatively high conductivity and a relatively low activation energy for conduction. Evidently the impurity atom concentration may be high enough to result in degeneracy. Conventional 50-kV electron diffraction patterns of the surface of an octahedral crystal which had been exposed for an hour or so to boron carbide at high pressures and temperatures showed, in addition to an excellent crystalline diamond pattern, some extra spots corresponding to a (200) reflection which is not usually seen for diamond. These extra spots could be interpreted as arising from the presence of extra atoms, presumably of boron, arranged

in regular fashion in the normal, relatively large, interstitial cavities of the diamond lattice.

Although nitrogen is known to be present in many diamonds^{7,8,9} its presence does not give rise to *n*-type semiconduction, and *n*-type semiconducting diamonds are at best extremely rare.

However, it has been found that both *n*-type and *p*-type diamonds may be prepared by suitable ionic bombardment of diamonds. The preparation and some of the properties of such crystals are discussed below.

II. EXPERIMENTAL PROCEDURE

The diamonds to be bombarded with ions were placed in a shallow metal cup about 2 cm in diameter inside a bell jar, as shown in Fig. 1. This cup was made the cathode. The anode was a metal disc about 1 cm above the cup. Usually the anode and cathode were made of molybdenum or nickel. The region inside the bell jar was pumped down to a few microns pressure and then selected gases were passed through the jar via controlled leak so as to maintain a nearly constant pressure while pumping. A direct current of a few dozen milliamperes at a potential of 1500–2800 V maintained

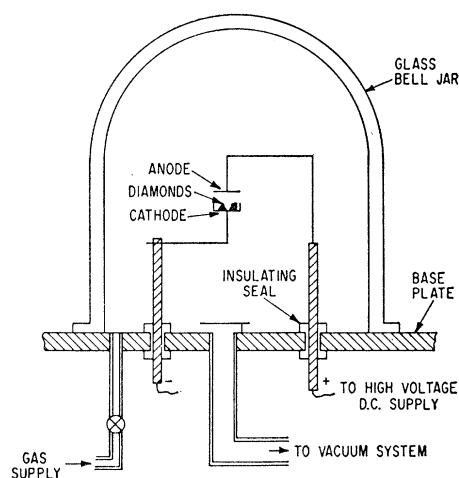


FIG. 1. Ionic bombardment apparatus.

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⁵ R. H. Wentorf, Jr. and H. P. Bovenkerk, *J. Chem. Phys.* **36**, 1987 (1962).
⁶ H. P. Bovenkerk, F. P. Bundy, H. T. Hall, H. M. Strong, and R. H. Wentorf, Jr., *Nature* **184**, 1094 (1959).

⁷ W. Kaiser and W. L. Bond, *Phys. Rev.* **115**, 857 (1959).
⁸ C. M. Huggins and P. Cannon, *Nature* **194**, 829 (1952).
⁹ H. J. Milledge and H. O. A. Meyer, *Nature* **195**, 171 (1962).

a glow discharge in the ionized gas between anode and cathode. The ions struck both the cathode and the diamonds on it, and metal was sputtered onto the diamonds. After an hour or so of bombardment, the current was turned off and the diamonds were removed from the cathode. Any metal coating was easily removed by hot aqua regia followed by washing with distilled water.

Several kinds of natural diamonds as well as synthetic diamonds were treated, with similar results. However, all of the data reported in this paper were taken from measurements made upon natural white octahedral diamonds about 1.2 mm on edge. The convenient size and uniform quality of these crystals made them preferable for study.

The electrical resistances of the treated diamonds were measured between silver or phosphor bronze electrodes using a Kiethley Model 610A electrometer. Whether a given crystal was *n* or *p* type could be easily determined by heating the top electrode and noting the voltage developed across the crystal; the sign of the charge on the cooler electrode is the same as the type.

III. EXPERIMENTAL FINDINGS

It was soon apparent that the electrical conductivities of all the 8 faces of a crystal were not the same. The uppermost face, which received the most direct ionic bombardment, had the lowest resistance, and the face which had lain next to the cathode generally showed a resistance as high as that of untreated diamond, e.g., $10^{11} \Omega$ or more between electrodes 1 mm apart. The remaining 6 inclined faces had intermediate resistances. When such a diamond was placed between a pair of flat electrodes its over-all resistance depended on which faces happened to be against the electrodes, but there were usually several positions for which the average resistance was nearly the same, and these positions were used for the data in this paper.

It was found that the treated diamonds had average resistances of 10^5 to $10^{10} \Omega$ at 25°C, depending on the treatment to which they had been exposed. The crystals which had been exposed to bombardment in an atmosphere of nitrogen or argon (known to contain about 0.1% each of N_2 and O_2) were *n*-type semiconductors. Those bombarded in an atmosphere of hydrogen were found to be *p* type and those bombarded in helium or oxygen did not produce high enough thermoelectric voltages for their type to be determined even though their resistances were in the same range as for diamonds bombarded in nitrogen. The kind of metal used for electrodes during bombardment did not seem to have a noticeable effect on the electrical behavior of the treated diamonds.

A plot of the resistance-temperature behavior of the treated diamonds is shown in Fig. 2. The various treatments, the type, and the average activation energy

for conduction of the crystals are also indicated. Usually the thermoelectric powers were about $10 \mu V/^\circ C$.

Several of the treated diamond surfaces were examined in this laboratory using standard 50 kV electron diffraction techniques. The electron diffraction patterns showed that the lower the resistance of a face, the lower its crystalline perfection. An untreated face showed excellent crystalline perfection with many Kikuchi lines. A face which had been normal to the stream of ions showed very little crystalline perfection; the diffraction-pattern consisted of diffuse rings. Intermediate faces yielded diffraction patterns indicating intermediate crystalline perfection, according to the direction and number of bombarding ions. In these studies the electrons were diffracted from surface layers about 100 Å deep.

The diamond surfaces which had been exposed to ion bombardment had a light brownish-gray color whose intensity varied directly with the amount of exposure of the surface to the bombarding ions. Thus the uppermost faces of the diamond crystals were the most intensely colored and the bottom face which had rested against the cathode had no noticeable surface coloration.

When a previously bombarded and cleaned diamond was buried in graphite and exposed to a pressure of 63 kbars and temperature of about 1700°C for 12 min, then mechanically cleaned, its resistance was found to be about $10^{11} \Omega$ or higher and electron diffraction patterns of its surfaces indicated mostly crystalline diamond.

A hot (210°C) mixture of H_2SO_4 and KNO_3 is known to oxidize most graphite in a few minutes but is much slower to act on diamond. When treated diamonds were exposed to a hot H_2SO_4 and KNO_3 mixture for several minutes and then washed and dried, it was found that their characteristic color was somewhat reduced and their average resistances and activation energies for conduction had increased. However, even after an hour's treatment with hot H_2SO_4 and KNO_3 mixture, a bombarded diamond crystal still had an average resistance of about $10^{10} \Omega$ at 25°C. Electron diffraction patterns of its surface showed that the crystallinity of its surface had noticeably increased, but still did not match that of untreated diamond. Some broad spots appeared in the electron diffraction patterns. The spacings of the spots indicated lattice parameters of 3.56 to 3.70 Å. (Plain diamond showed 3.56 Å.) A nitrogen-bombarded diamond, originally *n* type, remained *n* type after the acid treatment. But a helium-bombarded diamond, which before acid treatment had shown no detectable thermoelectric power, showed a small thermal emf indicating a *p*-type semiconductor after acid treatment.

When a diamond crystal, made semiconducting by ion bombardment, was cleaned and then heated for an hour or so in air to 300–400°C, the light brown surface

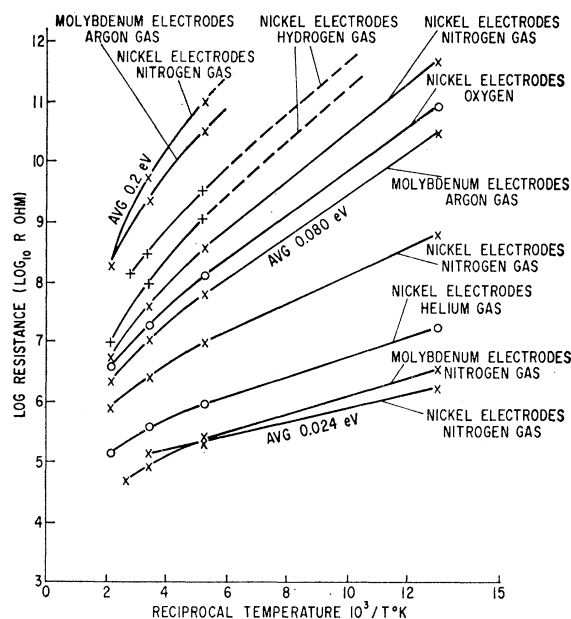


FIG. 2. Plot of \log_{10} resistance of bombarded diamonds vs reciprocal temperature.

coloration was reduced and the average resistance of the diamond was increased by a factor of 10 to 1000.

IV. REMARKS

It is evident from the observations reported above that the electrical conductivity of the ion-bombarded diamonds is mainly due to a thin surface layer of matter on the crystals. The electron diffraction studies indicate that this conducting surface layer is not nearly as perfectly crystalline as ordinary diamond. Instead the surface crystallinity appears to have been more or less destroyed or disrupted by the bombarding ions. In addition to the disruption, it appears that some of the bombarding atoms are trapped in the surface layers and thereby create donors or acceptors for electrical conduction, because the predominant type of carrier depends on the kind of gas ions used for bombardment. Whether the electrons or holes are provided by the gas atom or by partially bonded carbon atoms near a gas atom is still mostly a matter for speculation. Obviously vacancies, or substitutional or interstitial atoms of various kinds are likely to exist in the disrupted surface layers.

It was surprising to find that the thermoelectric powers were so small for diamonds bombarded in the presence of oxygen or helium. This could be explained by assuming that both *p*-type and *n*-type regions are produced in the surface layers, but that there are many of them and they are arranged in random fashion to form a complex series-parallel electrical network whose over-all characteristics would be neither *p* type nor *n* type.

A consideration of Fig. 2 shows that the higher the resistance, the higher the activation energy for conduction. The higher resistance is also associated with a somewhat greater degree of crystalline perfection. Evidently the greater the degree of crystalline perfection, the fewer are the conducting states and the more distant in energy they lie from the valence or conduction bands. The results of the oxidation treatments with H_2SO_4 and KNO_3 , and the heating in air indicate that the surface layers responsible for the color and the conductivity are not made of a stable crystalline form of carbon, but instead seem to be a particular sort of amorphous carbon derived from diamond.

The bombardment effects were not particularly noticeable with diamond when the total potential drop between the anode and the cathode was kept below about 1500 V during bombardment. Although the distribution of energy among the bombarding ions of the discharge was not known in this work, it appears that the bombarding ions must possess a "threshold energy" in order to affect the diamond surface significantly; ions having too little energy apparently have very little effect. Evidently, the necessary energies lie above those normally found suitable for cleaning surfaces in high vacua.¹⁰

Diamonds which have been heavily exposed to neutrons are known to contain many carbon atoms which have been displaced from their normal lattice positions.^{11,12} Such diamonds are often strongly colored brown or green as a result of the neutron irradiation, but their electrical conductivities have not been reported to be substantially different from that of ordinary diamond. Perhaps more extensive disruption of the crystal is necessary before the electrical conductivity is as strongly affected as it was in the experiments of this paper.

So far the coloration and enhancement of electrical conductivity produced by ion bombardment have been observed only in diamond. It may be that these effects are most easily produced in strong, refractory substances which have relatively wide energy gaps between their valence and conducting bands. Such states of matter may be interesting because they would represent particular kinds of "amorphous" matter which owe their unique properties to certain kinds of special structures or arrangements of atoms.

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