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Rectification, Photoconductivity, and Photovoltaic Effect in Semiconducting Diamond*

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Studies of the rectification between a metal point and *p*-type semiconducting diamond show that the formation of the potential barrier is essentially independent of the work function of the metal. The rectifying barrier apparently is formed by the establishment of equilibrium between charges in surface and interior states as proposed by Bardeen for the case of silicon. The semiconducting diamonds are photoconducting in the ultraviolet and visible regions with the maxima occurring at 224, 228, 640, and 890 mμ. Generally, diamonds have not been observed to be photoconducting in the visible region; however, it has been observed that in some cases an enhancement of conductivity induced by ultraviolet radiation results upon simultaneous irradiation with red light. There is agreement between the spectral response of photoconductivity and photovoltages developed at metal contacts with the exception that photovoltages developed near 440 mμ were not obtained in photoconductivity.

I. INTRODUCTION

THE early investigations of the physical properties of diamond by Robertson, Fox, and Martin[1] disclosed the possible existence of two types, designated as Type I and Type II. The separation of diamond into two types was based primarily on differences in their optical absorption spectra, photoconductivity, birefringence, and x-ray diffraction. According to their classification, Type I diamonds exhibit strong infrared absorption in the 2 to 6μ and 8 to 13μ regions. Type II diamonds do not show the 8–13μ band in the infrared. Photoconductivity produced by ultraviolet radiation is considerably less in Type I diamonds than in Type II diamonds.

Custers[2] distinguished further differences in the Type II diamonds and proposed the division into two groups designated as IIa and IIb. The Type IIb diamond has a characteristic luminescence when irradiated with ultraviolet light in the region of 2500 A and conducts electricity. Type IIa does not exhibit the property of luminescence and is a good insulator. Subsequent investigations[3] have shown that the properties of these unusual conducting diamonds are characteristic of impurity activated semiconductors; however, this has not been definitely established. The purpose of this investigation is to extend the knowledge of the properties of semiconducting diamonds from studies of rectification, photoconductivity, and the photovoltaic effect.

The two diamonds used in our investigation originated from the Premier Mines in South Africa and have properties characteristic of the Type IIb diamond, i.e., both show luminescence on irradiation with ultraviolet light and are conductors of electricity. The diamond of lower conductivity is a rectangular parallelepiped of dimensions 2.2×3.5×6.5 mm. One end of the diamond is faintly blue; the remainder of the crystal is practically free from coloration as distinguished with the eye. The room temperature resistivity of the blue end is about 65 ohm cm and of the clear end is 3.6×10^5 ohm cm. Hall measurements conducted on the specimen show that it is a *p*-type semiconductor. The second diamond, which is irregular in dimensions, has a more intense blue color than the other diamond and a higher electrical conductivity. The slope for the dependence of $k \ln R$ on $1/T$ as determined by Smoluchowski and Leivo[4] was found to be 0.35 electron volt at room temperature, where R is the resistance, T the absolute temperature, and k the Boltzmann constant.

II. RECTIFICATION AT METAL-DIAMOND CONTACT

Rectification studies were carried out to determine whether the rectification between a metal point and the diamond was dependent upon the work function of the metal. In the case of silicon and germanium, Meyerhof[5] found that the rectification is largely independent of the work function of the metal. The lack of dependence of the rectification upon work function was explained by Bardeen[6] on the basis of surface states. Similar to silicon, no significant dependence upon work function existed, thus indicating that surface states in diamond are responsible for developing the potential barrier.

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† Now with Phillips Petroleum Company, Bartlesville, Oklahoma.

[1] Robertson, Fox, and Martin, Trans. Roy. Soc. (London) **A232**, 463 (1934).

[2] J. F. H. Custers, Physica **18** 489 (1952); Physica **20**, 183 (1954).

[3] R. Smoluchowski and W. J. Leivo, Phys. Rev. **98**, 1532(A) (1955); R. Wolf and J. Woods, Phys. Rev. **105**, 921 (1957); J. F. H. Custers, Nature **176**, 173 (1955), and **176**, 360 (1955); J. J. Brophy, Phys. Rev. **99**, 1336 (1955); Stein, Bell, and Leivo, Bull. Am. Phys. Soc. Ser. II, **1**, 127 (1956); M. D. Bell and W. J. Leivo, Bull. Am. Phys. Soc. Ser. II, **1**, 382 (1956), and Bull. Am. Phys. Soc. Ser. II, **2**, 171 (1957); H. B. Dyer and P. T. Wedepohl, Proc. Phys. Soc. (London) **B69**, 410 (1956); I. G. Austin and R. Wolfe, Proc. Phys. Soc. (London) **B69**, 329 (1956); P. T. Wedepohl, Proc. Phys. Soc. (London) **B70**, 177 (1957).

[4] R. Smoluchowski and W. J. Leivo, Phys. Rev. **98**, 1532(A) (1955).

[5] W. E. Meyerhof, Phys. Rev. **71**, 727 (1947).

[6] J. Bardeen, Phys. Rev. **71**, 717 (1947).

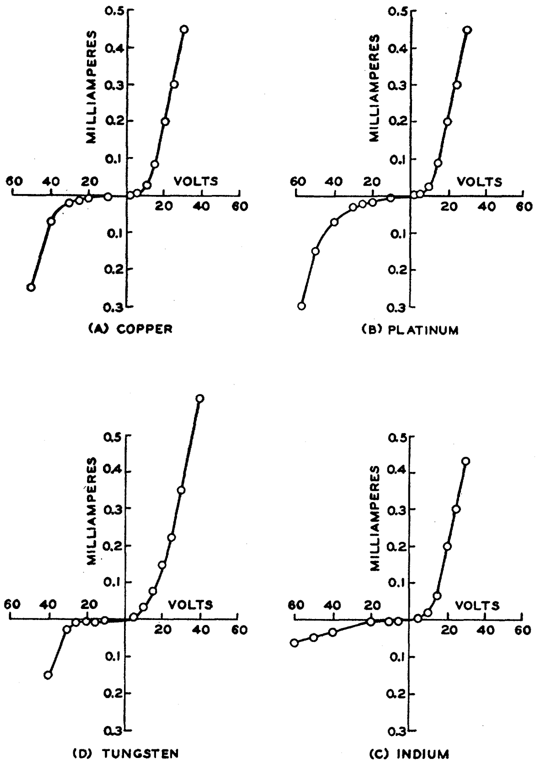
(A) COPPER

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Fig. 1. Rectification between semiconducting diamond and metal points of varying work function. All the curves are for a diamond having a relatively high electrical conductivity.

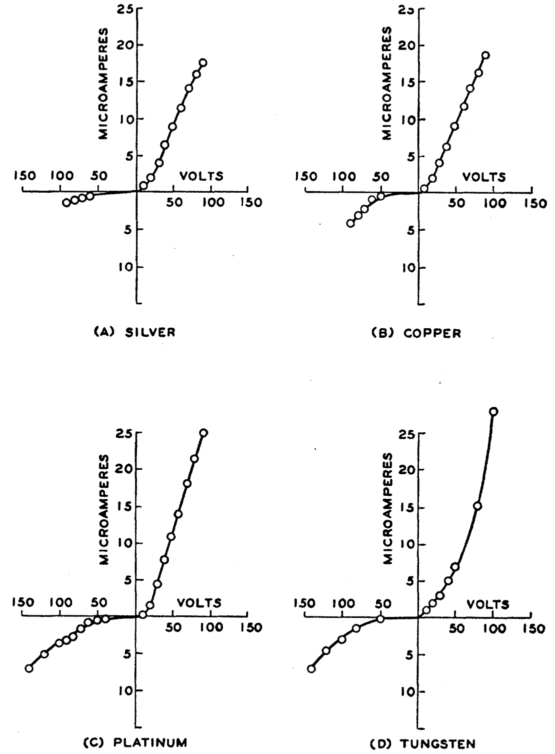
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Fig. 2. Rectification between different metal points and a semiconducting diamond having a relatively low electrical conductivity.

The point contact rectification characteristics of both diamonds were determined under direct current conditions. Metals used for the point contact were, in the order of increasing work function, indium, aluminum, copper, tungsten, silver, and platinum. The dependence of the rectifying properties of the diamonds on the work function of the metal used as the point contact is shown in Figs. 1 and 2. The curves in Fig. 1 are characteristic of the diamond of higher conductivity, and those of Fig. 2 show the rectification characteristics of the diamond of lower conductivity. The reverse characteristics of Fig. 1 show that break-down begins at approximately 30 volts for the higher conducting diamond. Reverse breakdown for the diamond of lower conductivity occurs between 50 and 60 volts. The direction of easy flow (forward bias) occurred when the diamond was positive with respect to the metal point. The curves of Fig. 2 were obtained with the point contact at the same position on the diamond of lower conductivity.

The measurements on the rectification properties of the diamonds indicate that the work function of the metal used as the point contact has negligible effect in forming the rectifying barrier. According to diode rectification theory and assuming that the potential barrier arises from the difference in work functions, the current is given by

$$I=Ae^{(\psi_s-\psi_m)/(kT)}(e^{qV/(kT)}-1)\equiv I_s(e^{qV/(kT)}-1), \qquad (1)$$

where A is a constant, ψ_s and ψ_m are the work functions of the semiconductor and the metal, k is the Boltzmann constant, q the electronic change, V the applied potential,[7] and T is the absolute temperature. If the rectification current is dependent upon the work function, as given by Eq. (1), the reverse saturation current I_s should vary by a factor of at least 10^8. From the curves it can be seen that the variation is less than a factor of 10. Metals of both high and low work functions give considerable rectification and show variations in the degree of rectification over the surface of the diamond. The variations over the surface are shown in Fig. 3 for a copper point contact on the diamond of higher conductivity. Rectification measurements were obtained in the temperature range 25°C to 300°C. At 300°C fairly good rectification curves were still obtained as shown in Fig. 4.

During the measurement of the rectifying properties it was observed that upon application of 45 volts to the point contact, in the direction of forward bias, the

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[7] In comparing the rectification curves, the applied voltage V is not the actual voltage across the rectifying barrier. The applied voltage is reduced by the "spreading resistance" which includes the conductivity of the specimen. See H. C. Torrey and C. A. Whitmer, *Crystal Rectifiers* (McGraw-Hill Book Company, Inc., New York, 1948), p. 83.

diamond of higher conductivity developed an intense blue luminescence which appeared to vary in intensity throughout the diamond. Light also appeared at the point contact. Electroluminescence has been observed in other specimens of semiconducting diamond.[8]

III. PHOTOCONDUCTIVITY

The spectral response curves for photoconductivity were determined at room temperature using a light source chopped at a frequency of 480 cps. After amplification, the spectral photoresponse was automatically recorded. Photoconductivity measurements were obtained on the diamond of lower conductivity in the ultraviolet, visible, and infrared regions of the spectrum. Since visible differences in the blue color of different portions are observable, the diamond was divided into five equal sections by successive masking of the surface, as indicated in Fig. 5. Photoconductivity measurements were made on each section. Measurements in the visible and infrared regions were taken without previous activation of the diamond with ultraviolet radiation. The spectral photoresponse of the photoconductivity is expressed as the relative photocurrent per photon of incident radiation.

The visible and infrared response of the blue portion of the diamond (Sec. *A*), is less than that of the clear portion near the center of the diamond (Sec. *B*). The peak response is broad and located at approximately 600 mμ as shown in curve *A* of Fig. 5. In this section of the diamond there is no detectable photoconductivity in the ultraviolet with the electric fields employed. Curve *B* of Fig. 5 shows the increased photoresponse in the visible and infrared obtained in a relatively clear portion (Sec. *B*) of the diamond. The peak response of the curve occurs at 630 mμ. As in Sec. *A* there is no detectable photoconductivity in the ultraviolet.

The visible response of Sec. *C* (not shown) is similar in response to *B*, but the photocurrent is greater. A peak occurs in the visible at 630 mμ. Section *C* is the first to show photoconductivity in the ultraviolet region, as shown in curve 5 of Fig. 6. The ultraviolet response is broad and occurs in the region 220 mμ to 240 mμ.

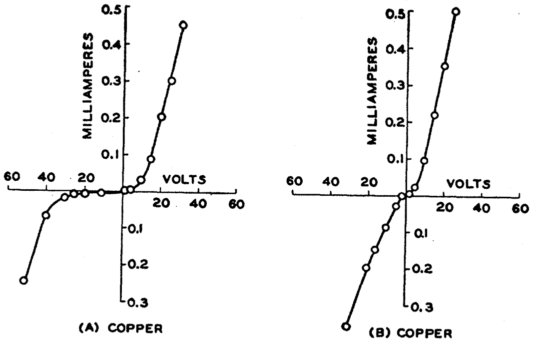

FIG. 3. Rectification between a metal point and a semiconducting diamond for various positions over the surface of the diamond.

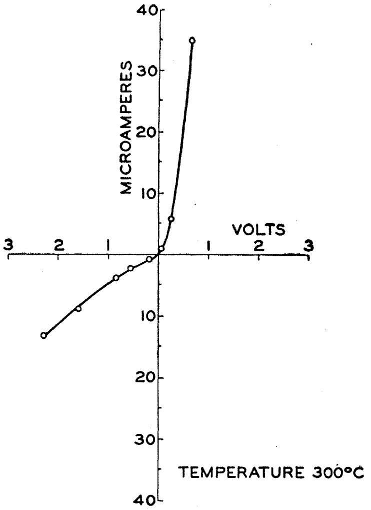

FIG. 4. Rectification between a metal point and a semiconducting diamond at a high temperature.

The photoconductive response of Sec. *D* is shown in curve *D* of Fig. 5. A peak is present at 640 mμ in the visible region. Subsequent measurements in this portion of the diamond gave indications of a second peak at 890 mμ in the infrared. There is an increased response to ultraviolet radiation in the section as shown in curve 6 of Fig. 6. Two peaks occur with maximum response near 228 mμ and 224 mμ.

Section *E* has a reduced photoresponse in the visible and infrared; also, no photocurrent could be detected in the ultraviolet. The response in the visible and infrared has two peaks at 640 mμ and 890 mμ which corresponds to 1.94 ev and 1.39 ev, respectively. The results of the above measurements of the photoconductivity in the diamond of lower conductivity are shown in Table I.

Definite indications of two peaks in the ultraviolet were obtained in subsequent measurements as shown in

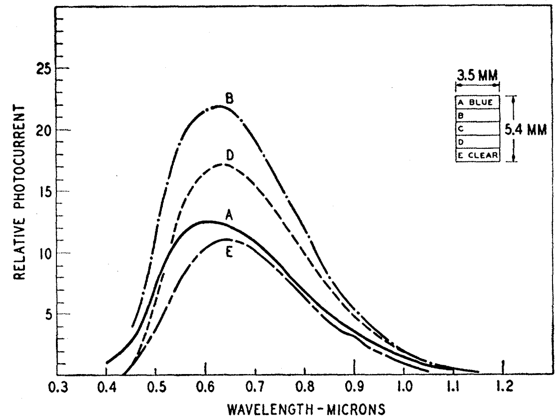

FIG. 5. Photoconductivity in various sections of a semiconducting diamond for the visible and infrared regions. Each curve represents the corresponding section of the diamond shown in the inset drawing.

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[8] R. Wolf and J. Woods, Phys. Rev. **105**, 921 (1957).

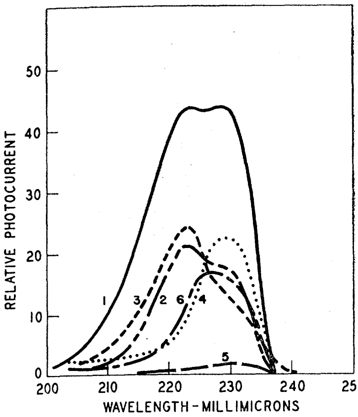

FIG. 6. Ultraviolet-induced photoconductivity in semiconducting diamond.

curves 1, 2, 3, and 4 of Fig. 6. The entire crystal was irradiated to obtain curve 1. Curve 2 is characteristic of the lower third portion of the diamond (clear end) scanned from long to short wavelength. Scanning the same portion from short to long wavelength gives curve 3. Curve 4 was obtained when the central third of the diamond was irradiated. Curves 5 and 6 correspond to Secs. *C* and *D* of Fig. 5. Peaks occurred near 224 mμ and at 228 mμ. The peak at 224 mμ varied in position and was not detected in all measurements as shown in curve 4. In the spectral regions 250 mμ to 350 mμ and 1.8μ to 12μ, there was no detectable photoconductivity at room temperature with the electric fields employed.

IV. PHOTOVOLTAIC EFFECT

The photovoltaic effect was observed in the diamonds in the visible and infrared using a light source chopped at 480 cps. The photovoltages generated in the diamond of lower conductivity show maximum response at 440 mμ and 640 mμ, with a minor peak at 890 mμ (Fig. 7). The two peaks at 640 mμ and 890 mμ correspond to those observed in the photoconductivity; however, the peak at 440 mμ was not detected in photoconductivity. All photovoltaic measurements in the long wavelength regions were taken with no previous activation of the diamond by ultraviolet radiation. Measurements in the ultraviolet region on the diamond of higher conductivity give the maximum response near 230 mμ. A photovoltaic effect was not detectable in the region 1.3μ to 12μ at room temperature. The spectral response of the photovoltage is expressed as relative photovoltage per photon.

TABLE I. Photoconductivity response in different sections of a semiconducting diamond.

Section	Color	Resistivity (ohm cm)	Visible and infrared response	Ultraviolet response
A	Blue	65	Broad peak at 600 mμ	None
B	Partially blue	· · ·	Peak at 630 mμ	None
C	Relatively clear	· · ·	Peak at 630 mμ	Slight response; 220 mμ to 240 mμ
D	Clear	3.6×10^5	Peaks at 640 mμ and 890 mμ	Good response; peaks at 228 mμ and 224 mμ
E	Clear	3.6×10^5	Peaks at 640 mμ and 890 mμ	None

The preceding measurements on the photovoltaic effect used a chopped light source in measuring the photovoltages developed; however, a constant light source was also used to illuminate the potential barrier between a metal point and the diamond of higher conductivity. Measurements were taken using a vibrating reed electrometer. The diamond was illuminated near the point contact using the desired radiation from a tungsten lamp or a quartz mercury arc.

The polarity of the photovoltage changed over the surface of the diamond. Also, at certain positions on the surface of the diamond the polarity changed sign on changing the light source from the full spectrum tungsten light to the full spectrum mercury arc. For example, the diamond was positive with respect to the metal point when irradiated with the tungsten source, but was negative when exposed to the mercury arc. The process appeared to be completely reversible. This effect was not observed over the entire surface.

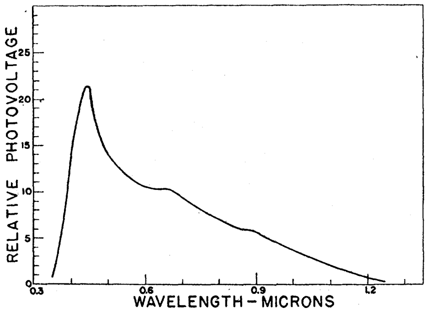

FIG. 7. Photovoltaic effect at metal-diamond interface.

The dc measurements were complicated by the polarization of the diamond upon illumination of the point contact. On continued irradiation of the diamond, the photovoltage would decrease to zero, and on interrupting the light, the photovoltage gave a deflection in the reverse direction. It was necessary to wait several hours before optimum response could again be obtained. The magnitudes of the photovoltages generated were of the order of 0.4 volt with the mercury arc and 0.1 volt using the tungsten source.

V. DISCUSSION

A. Rectification

The results of the rectification studies show that the work function of the metal has negligible effect in forming the rectifying barrier. Consequently, the barrier apparently is formed by establishing equilibrium between surface states and the interior of the diamond. The surface states indicated by our results must be such that the energy bands are depressed as they approach the free surface of the crystal. The existence of surface states may be caused by adsorbed atoms, crystal imperfections, or impurities near the surface, although their exact nature is not known. Shockley[9] has predicted surface levels on diamond that are half filled and which would allow surface conductivity to occur. The rectification curves at higher temperatures indicate that the useful range of elemental semiconductors may be extended.

B. Photoconductivity

Robertson, Fox, and Martin[1] observed photoconductivity in diamonds in the ultraviolet and they also found the photoconductivity could be enhanced by simultaneous irradiation of the crystal with red light. However, they did not obtain photoconductivity with red light alone. Specimens used in this investigation were photoconducting in the visible without simultaneous or previous irradiation with ultraviolet light.

Several recombination lifetimes may be expected to be present in a complex physical situation as that existing in semiconducting diamond. The magnitudes of the photocurrents obtained with a constant light source are different from those obtainable with a chopped light source because of the lifetimes of the carriers involved. Carrier lifetimes which affected the equilibrium dark current for several hours were present, as well as those responsible for the ac response with lifetimes less than the period of the chopped light source.

The change in magnitude of the photoresponse in various regions of the diamond, as shown by the curves in Fig. 5, is partially the result of determining the photoresponse under the condition in which a constant dark current is present in the crystal. Consequently, since the resistivity varies through the diamond, the magnitude of the electric field across each section is different when the current is constant. Thus, the resulting electric field in the blue portion of the diamond would be very small since the clear region has a much larger resistivity. It is not possible to obtain an accurate value of the resistivity in the various sections without cutting the diamond, and the use of potential probes would also alter the experimental conditions.

C. Photovoltaic Effect

In general, one can expect a close correlation between the spectral response in photoconductivity and the photovoltaic effect. However, one may also expect differences to occur because the photovoltaic effect is a surface phenomenon and the photoconductivity, in a region of considerable optical transparency, can be a bulk property. Different types of energy states existing at the surface and in the interior will affect the spectral response.

The measurements of the photovoltaic effect as a function of activating wavelength, in the visible and infrared, are in accord with the photoconductivity spectral response. Peaks at 640 mμ and 890 mμ in the spectral response of the photovoltaic effect correspond to peaks found in the photoconductivity. The peak at 440 mμ was not detected in photoconductivity measurements and could possibly be associated with energy levels formed by crystal defects corresponding to the electroluminescence observed in IIb diamonds.

The observed polarization, which reduces the photovoltaic response to zero on continued illumination, is probably the result of the immobilization of current carriers by trapping at crystal imperfections or at the electrodes. The polarity change of the photovoltage at different positions on the surface of the crystal can be explained if certain regions of the surface exhibit impurity band conduction, whereas, in other regions this does not occur.

At the present time several energy level schemes can be obtained which could be considered consistent with the results obtained from optical absorption, photoconductivity, photovoltaic effect, Hall effect, and the temperature dependence of resistivity. In particular, an acceptor level with an activation energy of 0.35 ev agrees well with experimental results. This would correspond to a group III impurity. Also, an intrinsic energy gap of 5.32 ev for diamond may be obtained from the ultraviolet response of the photoconductivity. However, considering multiple valence bands, and the various possible crystal imperfections, it is premature to establish the origin of the various energy levels without strong speculation.

ACKNOWLEDGMENT

We thank Dr. J. F. H. Custers, Director of Research, Diamond Research Laboratory, Johannesburg, for furnishing the specimens of semiconducting diamond and for the assistance he has given us in the work.

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[9] W. Shockley, Phys. Rev. **56**, 317 (1939).