

# Adsorption and Bonding Properties of Cleavage Surfaces of Bismuth Telluride\*

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No measurable adsorption of oxygen, nitrogen, or carbon monoxide was found for any of the clean surfaces produced. Water vapor had a very low sticking coefficient of the order of  $10^{-5}$ . The results are discussed in terms of the chemical bonding of bismuth telluride. It is concluded that the atoms on cleavage faces are in a saturated-bond condition.

## I. INTRODUCTION

IN recent years much information has been obtained concerning the physical properties of bismuth telluride. However the nature of the bonding between the atoms has not been established with certainty. Drabble and Goodman<sup>1</sup> have critically discussed various bonding theories proposed for bismuth telluride, and have advanced a model which is stated to be free of some of the objections applicable to earlier theories. However, much of the evidence concerning bonding is somewhat indirect. By studying the adsorption of gases on cleavage surfaces of  $\text{Bi}_2\text{Te}_3$  it is possible to obtain direct experimental evidence concerning the nature of the bonding of the atoms occupying these surfaces. The results turn out to be in full agreement with the theoretical model of Drabble and Goodman. It is appropriate to describe this model briefly before giving the experimental details.

## II. ATOMIC BONDING IN BISMUTH TELLURIDE

The bismuth telluride structure may be considered as a stack of 5-layer leaves. Each layer consists of only one type of atom. The layers, which are parallel to (0001) planes (the structure being regarded as hexagonal) occur in the order  $\text{Te}'\text{-Bi-Te}''\text{-Bi-Te}'$ . It is clear that there are two different environments for the Te atoms. The atoms designated as  $\text{Te}''$  are surrounded almost octahedrally by six Bi atoms while the  $\text{Te}'$  atoms have three nearest-neighbor Bi atoms in the same leaf and the next-nearest atoms are three  $\text{Te}'$  atoms in the adjacent leaf. Drabble and Goodman point out that the bond length between  $\text{Te}'$  atoms in adjacent leaves (3.57Å), is of the same order as the bond length between Te atoms in adjacent chains of the tellurium structure (3.74Å), and these bonds are usually assumed to be of the van der Waals type. This would imply that the electron density in the bonds between the leaves is effectively zero. Thus the four 5p valence electrons of the  $\text{Te}'$  atoms are used only in bonding to the three nearest-neighbor Bi atoms, i.e., in three nearly perpendicular bonds. The two 5s electrons are assumed to form a lone pair.

On this scheme one can explain the observed easy cleavage of  $\text{Bi}_2\text{Te}_3$  along (0001) planes by postulating that the cleavage occurs between the weakly bonded leaves. Only the  $\text{Te}'$  planes are then exposed.

## III. EXPERIMENTAL RESULTS ON ADSORPTION OF GASES

Single crystals of  $\text{Bi}_2\text{Te}_3$ <sup>2</sup> were cleaved in an ultra-high vacuum electron-diffraction tube so as to expose clean (0001) surfaces. The details of these experimental procedures are given elsewhere.<sup>3</sup> Low-energy electron-diffraction measurements indicated that the surface atoms occupied the same relative positions as those in bulk planes. Annealing experiments showed that the cleaved surfaces were largely free of distortion.

The surfaces were subjected to controlled exposures to various ambients. Any resulting changes were checked by noting changes in the electron-diffraction pattern after each exposure.

### A. OXYGEN

This gas was admitted from the atmosphere through a heated silver tube sealed to the vacuum system, and entered the experimental tube through a calibrated porcelain leak, while the tube was continuously pumped. Details of this method of admitting controlled amounts of gases have been given previously.<sup>4,5</sup> All parts of the tube were at room temperature during exposure. After an exposure, sufficient time was allowed for the gas to be pumped out before the diffraction gun filament was switched on and the diffraction beams were measured.

This procedure was carried out for exposures ranging from  $6.5 \times 10^{-5}$  mm Hg min to as much as 228 mm Hg min. However, no significant change in the pattern was found after these exposures. This somewhat remarkable result was confirmed for several separate surfaces. Apparently oxygen does not chemisorb on the surface at room temperature, and its physical adsorption is so weak that it is desorbed at room temperature.

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<sup>1</sup> J. R. Drabble and C. H. L. Goodman, *J. Phys. Chem. Solids* **5**, 142 (1958).

<sup>2</sup> Kindly supplied by Dr. D. A. Wright, General Electric Company Research Laboratories, Wembley, England.

<sup>3</sup> D. Haneman, preceding paper [*Phys. Rev.* **119**, 563 (1960)].

<sup>4</sup> R. E. Schlier, *J. Appl. Phys.* **29**, 1162 (1958).

<sup>5</sup> D. Haneman, *Proceedings of Second Conference on Semiconductor Surfaces* (to be published).

### B. CARBON MONOXIDE AND NITROGEN

Carbon monoxide is known from omegatron studies to be, in many cases, the major component of the ambient in a high vacuum system. It is reported to have rather high adsorption rates on many surfaces, perhaps partly because the molecular bond need not be broken for chemisorption to take place. Since the latter property may have been an influence in preventing oxygen adsorption on the  $\text{Bi}_2\text{Te}_3$  surface, it was decided to study carbon monoxide adsorption.

A "Linde M.S.C." high-purity sealed flask of CO was attached to the system and the gas was admitted to the tube through the porcelain leak, using the same precautions as for oxygen. However, exposures up to 0.6 mm Hg min caused no observable change in the diffraction pattern, thus indicating a sticking coefficient of less than  $10^{-9}$ . This limit is so low that it is concluded that CO also does not adsorb on the surface at room temperature.

The same procedures were carried out using nitrogen from a "Linde M.S.C." high-purity sealed flask. No changes in the diffraction pattern were found after exposures of 1.5 mm Hg min indicating that nitrogen also does not adsorb at room temperature on the surface.

### C. OZONE EXPERIMENTS

Ozone was produced by exposing oxygen in the tube to the radiation from a 250-watt mercury discharge lamp (type General Electric U.A.2) mounted 1 cm from a 2.5-cm diameter quartz window sealed on a side arm of the tube. A strong odor of ozone was produced in the air surrounding the lamp. The ozone concentration inside the tube was measured by an omegatron. This indicated a value of less than 0.1% of the oxygen concentration. However, the concentration in front of the crystal may have been greater than this since ozone molecules would have made at least one collision in reaching this region instead of at least three in reaching the ionization region of the omegatron, with consequent enhanced decomposition probability.

After exposures at room temperature of up to  $6 \times 10^{-2}$  mm Hg of oxygen for 73 minutes (4.38 mm Hg min) in the presence of the ultraviolet radiation, no change in the diffraction pattern was observed with the crystal at 70°C during measurements. Although the precise exposure to ozone could not be determined, the evidence appears to indicate that the sticking probability of ozone on the surface was also very low.

### D. WATER VAPOR

In view of the negligible adsorption on the surface of the active gases mentioned above, trials were made with water vapor. It is difficult to let water vapor into a vacuum system with cold traps without admitting other gases. Since, however, these appeared to have little effect on the surface, the first experiments consisted in allow-

ing atmospheric air, containing the prevailing percentage of water vapor, to enter the tube and remain for about an hour. The tube was then pumped out for several days without baking. The ambient pressure with several tungsten filaments hot was about  $10^{-6}$  mm. Under these conditions the crystal surface was examined by electron diffraction. The original diffraction pattern was now practically extinguished. The strongest original beams were barely detectable, being about 0.1% of their former intensity.

The crystal was heated (by radiation) for 1.5 hours at 96°C in an ambient of about  $10^{-6}$  mm. Omegatron measurements showed that this was 60%  $\text{H}_2\text{O}$ , the bulk of the remainder being a gas of mass 28, mainly CO. After this heat treatment the original diffraction pattern was almost fully restored. The low regeneration temperature suggested that the major cause of the disappearance of the beams during exposure to the atmosphere was the water vapor. Further tests confirmed this indication.

Controlled exposures were then carried out as follows. A section of the glass wall of the tube (it had not been baked) was heated with a projection lamp to a temperature of about 150°C. This caused both water vapor and mass 28 gas to be liberated copiously and continuously, as measured by an omegatron. The glass was kept heated during the exposure with only the omegatron filament hot. Although the mass 28 gas was liberated faster than the water vapor, it was also pumped faster by the diffusion pumps. By keeping the tube continuously pumped during the exposure, it was possible to obtain an ambient consisting of 65% water vapor.

The diffraction beam intensities after exposures of  $3 \times 10^{-4}$  mm Hg min,  $6 \times 10^{-4}$  mm Hg min and  $6 \times 10^{-3}$  mm Hg min of  $\text{H}_2\text{O}$  were 80%, 65%, and 30%, respectively, of the intensities for an uncontaminated surface. These data indicate an initial sticking coefficient for water vapor on the surface of about  $10^{-5}$ .

### E. REGENERATION OF SURFACE

After adsorption of water vapor, the original diffraction pattern could be restored by heat treatment alone. Heating for 1.3 hours at a temperature as low as 50°C caused an increase in beam intensity from 33% of the original to about 45%. Heating at 110°C for three hours caused a full restoration of the original intensities. It is presumed that the water vapor is simply desorbed from the surface during heating.

### F. SECONDARY EMISSION

Some data, incidental to the main work, were obtained on secondary electron emission from a clean surface in the range of 20 to 250 ev primary electron energy. The coefficient of secondary emission for normal incidence rose approximately linearly from 0.25 at 20 ev to 0.79 at 250 ev.

## IV. DISCUSSION

The negligible adsorption of oxygen and carbon monoxide on the cleaved face of bismuth telluride is rather remarkable. The fact that the surface atoms show such low interaction with these active gas atoms and molecules could be explained if the bonds of the surface atoms (a) are saturated (no "dangling bonds") and (b) are directed into the interior, away from the surface. These conditions, however, are precisely those obtained by Drabble and Goodman regarding the bonding of the  $\text{Te}'$  atoms on the outside layers of the 5-layer leaves, as discussed in Sec. II. The experimental results are thus in good agreement with the following assumptions:

(1) On cleavage along (0001) faces, the exposed planes are those composed of the outside atomic layers of the 5-layer leaves.

(2) These outside layers, composed of  $\text{Te}'$  atoms, have only weak, van der Waals type bonds with the  $\text{Te}'$  atoms in the adjoining outside layers of the next leaves.

On the above scheme a satisfactory bond picture can be given which explains both the ready cleavage of  $\text{Bi}_2\text{Te}_3$  and the negligible adsorption of oxygen and carbon monoxide on the cleaved surfaces at room temperature.

The situation with respect to water vapor is interesting. There is at present little experimental information available about the adsorption of water vapor on clean surfaces. Hence, it is not known if this gas exhibits, in general, more adsorption on most clean surfaces than active gases like oxygen. For the case under consideration here, however, the fact that appreciable adsorption of water vapor was observed can be explained in terms of the above model in the following manner.

Although the nature of the bonds between water molecules in water is not known with certainty,<sup>5</sup> nevertheless, it is obvious that there must be some attraction between two such molecules at room temperature even

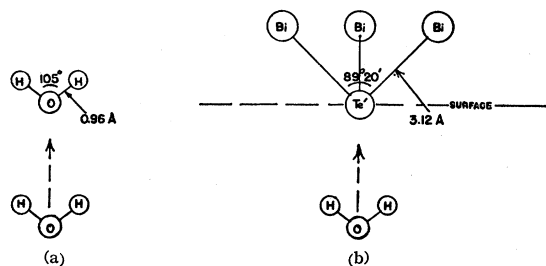


FIG. 1. Possible relative orientations when water molecule (a) combines with another water molecule, (b) adsorbs onto a  $\text{Te}'$  atom on (0001) surface of  $\text{Bi}_2\text{Te}_3$ .

<sup>5</sup> J. D. Bernal, Proc. Roy. Soc. (London) A247, 536 (1958).

TABLE I. Properties of (0001) cleavage surface of  $\text{Bi}_2\text{Te}_3$ .

Work function	$5.30 \pm 0.03 \text{ eV}^a$
Structure	Same as in bulk planes. Triangular, atomic spacing of $4.384 \text{ \AA}^b$
Surface bonding	Bonds saturated, and directed towards interior (Fig. 1)
Sticking coefficient for $\text{O}_2$	$\sim 0$
CO	$\sim 0$
$\text{N}_2$	$\sim 0$
$\text{H}_2\text{O}$	$\sim 10^{-5}$
Secondary emission	0.25 at 20 eV increasing linearly to 0.79 at 250 eV

<sup>a</sup> D. Haneman, J. Phys. Chem. Solids 11, 205 (1959).

<sup>b</sup> D. A. Wright, *Semiconductors and Phosphors* (Interscience Publishers, Inc., New York, 1958), p. 477.

though the atomic bonds in each molecule are saturated. There is then an interesting correspondence between the case of a water molecule attaching itself to another water molecule in the manner depicted in Fig. 1, and a water molecule attaching itself to a  $\text{Te}$  atom on a cleavage surface in  $\text{Bi}_2\text{Te}_3$ . In both cases the adsorber is a group 6 atom whose bonds are saturated, and directed away from the adsorbate molecule. From this correspondence one may postulate that the forces which cause a water molecule to adsorb onto an atom on a cleavage face at room temperature are similar in nature to those forces, as yet not fully determined, which cause it to attach itself to another water molecule at room temperature. Thus, it is possible that the adsorption of water vapor on cleavage surfaces of  $\text{Bi}_2\text{Te}_3$  is due to the particular properties of this interacting system, and hence the significant adsorption rate can be understood even though oxygen and other gases show negligible adsorption.

We now summarize in Table I some known surface properties of cleavage faces of  $\text{Bi}_2\text{Te}_3$ .

It may be noted that the cleavage surface of  $\text{Bi}_2\text{Te}_3$  is perhaps the only semiconductor surface for which the nature and positions of the bonds of the surface atoms would seem to be established. It may thus be a favorable example for which to perform theoretical calculations of surface parameters, including work function.

## V. ACKNOWLEDGMENTS

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