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Surface Structures and Properties of Diamond-Structure Semiconductors*

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Low-energy electron-diffraction and secondary electron-emission measurements have been made on (111) and (11$\bar{1}$) surfaces of GaSb and (100) surfaces of InSb. To account for the diffraction patterns observed both for these materials and previously for Ge and Si, a general model for (111) surfaces of diamond-structure semiconductors is proposed. Every second atom, counting along alternate close-spaced rows is raised with respect to its neighbors, being bonded to the sublayer by three p bonds while the "dangling bond" is s type. The remaining three-fourths of the surface atoms have dangling p bonds and are bonded to the sublayer by trigonal sp^2-type bonds.

The Ga or (11$\bar{1}$) face of GaSb has maximum sticking coefficients of 10^{-5} and 10^{-4} for oxygen and CO_2, respectively, these values being 10 times greater than those found for the Sb or (111) face. Multilayer adsorption of oxygen takes place on all the surfaces measured. The oxygen can be removed by heat treatment alone. Evidence is presented to show that diffusion of oxygen into the bulk is an important mechanism for regenerating the clean surfaces by heat treatment. Carbon dioxide adsorbs on GaSb so as to show structure. It apparently deposits as an unbroken molecule, and, unlike oxygen, does not build up several layers.

I. INTRODUCTION

PREVIOUS low-energy electron-diffraction measurements on surfaces of Ge, Si,[1] and InSb,[2] cleaned by the ion bombardment and annealing technique of Farnsworth *et al.*,[3] have indicated that the atoms in the surface layer occupy structures such that half-order diffraction beams are observed. The occurrence of such beams has been interpreted as showing that the surface atoms are displaced from their normal bulk positions. A model of such atomic displacements on (001) surfaces has been discussed by Schlier and Farnsworth. In this article we report results of low-energy electron-diffraction measurements on (111) and (11$\bar{1}$) surfaces (designation used previously[2]) of GaSb,[4] and on (001) surfaces of InSb. On the basis of results for all four abovementioned diamond-structure semiconductors, a model for a clean (111) surface is deduced which would appear to account for the observed results in a simple manner. A new model for an (001) surface is also suggested.

Adsorption of various gases on the clean surfaces has been measured using low-energy electron-diffraction and also secondary electron-emission measurements as monitors of the process. New evidence which throws light on the mechanism of regeneration by heat treatment of clean surfaces after oxygen adsorption is presented.

A difference between gas adsorption rates on (111) and (11$\bar{1}$) surfaces of GaSb has been found. Because of the asymmetry of the zinc-blende structure in the [111] direction, such faces [created by a cut parallel to (111) planes] consist ideally of Sb faces and Ga faces, respectively. The results are discussed in terms of the new surface models.

II. CRYSTAL PROCESSING AND VACUUM PROCEDURES

Measurements were made in a low-energy electron diffraction tube (assembled by Dr. R. E. Schlier) of a type described by Farnsworth *et al.*,[3] a separate experiment being performed for each crystal face. The crystal mount arrangement was the same as that described previously,[2] the crystal being pressed against a Mo block by spring-loaded Mo hooks bearing on slots cut in the crystal sides. All tube parts were degreased in an acetone extractor prior to assembly in the tube.

An n-type single crystal of GaSb, having an impurity content of 10^{16}/cc, and a single crystal of InSb having an impurity content of 10^{15}/cc were used. Specimens were cut in the form of cylinders 8 mm long and 7 mm in diameter. The front faces were oriented parallel to desired planes to within $\frac{1}{4}$ degree by an x-ray method. The faces were ground and polished, and etched. GaSb faces were immersed for a few seconds in a heated mixture of 2 parts 70% HNO_3, 1 part 50% HF, and 1 part glacial acetic acid, diluted with distilled water. The InSb face was etched in a solution (room temperature) of equal parts of HNO_3 and HCl diluted with distilled water.

The etching action was stopped by flooding with distilled water before removing the crystal face from the solution, in order to prevent very thick oxide layers being formed. Identification of the Ga and Sb faces of the GaSb crystals was made by correlating their different etch characteristics with the x-ray data of

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[1] R. E. Schlier and H. E. Farnsworth, J. Chem. Phys. **30**, 917 (1959).

[2] D. Haneman, J. Phys. Chem. Solids **14**, 162 (1960).

[3] H. E. Farnsworth, R. E. Schlier, M. George, and R. M. Burger, J. Appl. Phys. **29**, 1150 (1959).

[4] A summary of measurements on GaSb is given in Proceedings of International Conference on Semiconductor Physics, Prague, 1960 (to be published).

Warekois and Metzger.[5] The $(11\bar{1})$ face consists ideally of Ga atoms and the (111) face of Sb atoms.

III. CLEANING PROCEDURES

After the usual vacuum procedures, pressures of below 10^{-9} mm Hg were obtained in the experimental tube and were 2×10^{-9} mm with several filaments hot. All surfaces were cleaned by the ion-bombardment and annealing technique, it having been shown previously that this was efficacious for compounds[2,6] as well as for elements. Low current densities of 5 to 10 μa/cm^2 were used for periods of 5 to 20 minutes at ion energies of 200 to 600 ev. Full precautions were taken against the back-sputtering effect[2] by ensuring that the crystal face could "see" only metal surfaces (at grid potential) during ion bombardment. Argon pressures during bombardment were 10^{-3} to 10^{-4} mm Hg, the gun used to ionize the argon being shielded from the crystal by a Mo shield at the accelerating-grid potential of +50 volts with respect to the filament. No electron diffraction patterns could be obtained for the ion-bombarded surfaces, indicating a disordered structure. However, sharp diffraction patterns were obtained after annealing. For both the InSb (mp 523°C) and GaSb (mp 725°C), annealing at 350°C–400°C for 30 minutes or more was sufficient. At these temperatures no hillock formation[7] was observed on any of the surfaces.

IV. DIFFRACTION PATTERNS

Gallium Antimonide

Intense and reproducible low-energy electron-diffraction patterns were obtained from both (111) and $(11\bar{1})$ faces after the ion-bombardment and annealing cycles. The patterns were characteristic of (111) GaSb planes, using the bulk lattice constant of 6.09 A for GaSb. They were in general somewhat more intense on the $(11\bar{1})$ face than on the (111) face. On the latter face, beams in the (112) azimuth were weak compared to beams in the (110) azimuth.

Measurements in the (110) and (112) azimuths on both faces indicated that in addition to strong integral-order beams there were half-integral order beams of about one fourth to one half the intensity of the integral-order beams on the average. These characteristics applied to both (111) and $(11\bar{1})$ surfaces. A plot of beam positions in the (110) azimuth for a $(11\bar{1})$ face is shown in Fig. 1. A typical recorder trace of diffracted beam current versus primary electron energy for a clean surface is shown in Fig. 2(a).

Indium Antimonide

Reproducible diffraction patterns were obtained from the (100) face. The intensities of the patterns were in general about one third of those obtained previously[2]

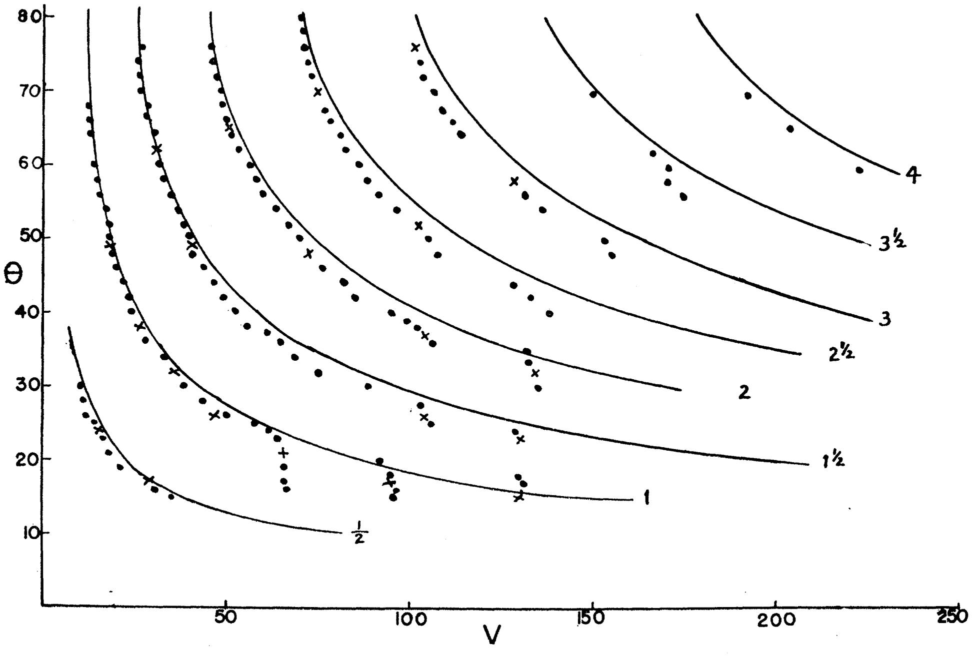

FIG. 1. Positions of diffraction beams in the (110) azimuth for a cleaned $(11\bar{1})$ surface of GaSb, plotted as a function of colatitude angle θ and primary beam voltage V. The solid curves are theoretical plots of the surface grating formula $n(150/V)^{\frac{1}{2}}=d\sin\theta$, using the bulk lattice constant of 6.09 A for GaSb. Dots (·) represent diffraction peaks and crosses (X) indicate positions at which the peaks are maximized. The order of diffraction, n, is marked on the curves.

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[5] E. P. Warekois and P. H. Metzger, J. Appl. Phys. **30**, 960 (1959).

[6] D. Haneman, Phys. Rev. **119**, 563 (1960).

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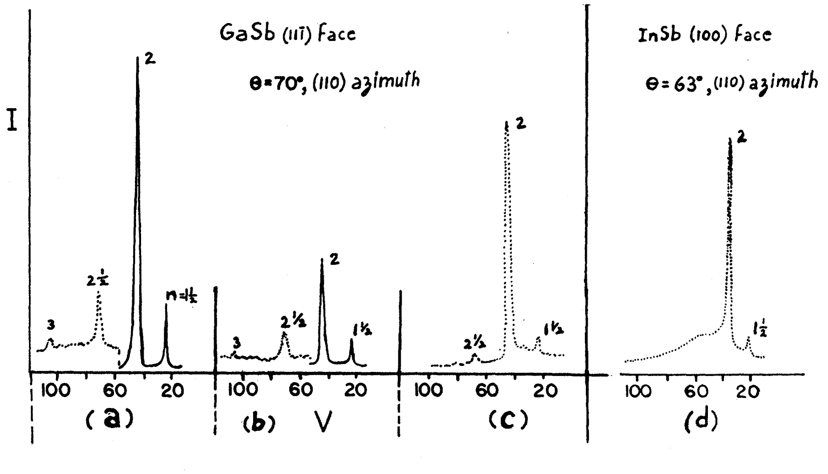

FIG. 2. Typical recorder traces of diffracted beam current I versus primary beam voltage V, in (110) azimuth. (a) Clean (11$\bar{1}$) GaSb surface (a); (b) surface (a) after exposure to 7×10^{-5} mm min of oxygen; (c) surface (a) after exposure to 7×10^{-2} mm min of carbon dioxide; (d) clean (001) InSb surface. Solid curves would be four times as high as shown if plotted to same scale as dotted curves.

for (11$\bar{1}$) faces. The patterns in the (310) azimuths were as intense as those in the (110) azimuths and about twice as intense as those in the (100) azimuths. Weak half-order beams (about 10% of intensity of integral order beams on the average) were observed in the (310) and (110) azimuths but no such beams could be detected in the (100) azimuth. This feature was also found on (100) faces of Ge and Si by Schlier and Farnsworth.[1]

V. OXYGEN ADSORPTION CHARACTERISTICS

Exposure of the clean surfaces to oxygen, admitted through a heated silver leak, resulted in a gradual weakening in intensity of all diffraction beams. Pressures used ranged from 10^{-5} mm to 10^{-2} mm. The changes in beam intensities were a function of exposure (pressure×time) and were not sensitive to the absolute pressure. Half-order and integral-order beams were weakened at the same rate on all surfaces. However in the case of GaSb the rates at which the beams weakened were markedly different for the (111) and (11$\bar{1}$) surfaces. Plots of beam intensity versus oxygen exposure are shown in Fig. 3. It is seen that the (11$\bar{1}$) surface, consisting ideally of Ga atoms, showed a higher adsorption rate than the (111) surface, consisting ideally of Sb atoms. The adsorption rate of the latter surface was similar, at lower exposures, to those reported previously[2] for cleaned InSb (111) and (11$\bar{1}$) surfaces. A typical recorder trace after oxygen adsorption is shown in Fig. 2(b).

For the InSb (100) face the rate of decrease of beam intensity with oxygen exposure after about half coverage was not very different from that found earlier[2] for (111) and (11$\bar{1}$) faces, as shown in Fig. 3.

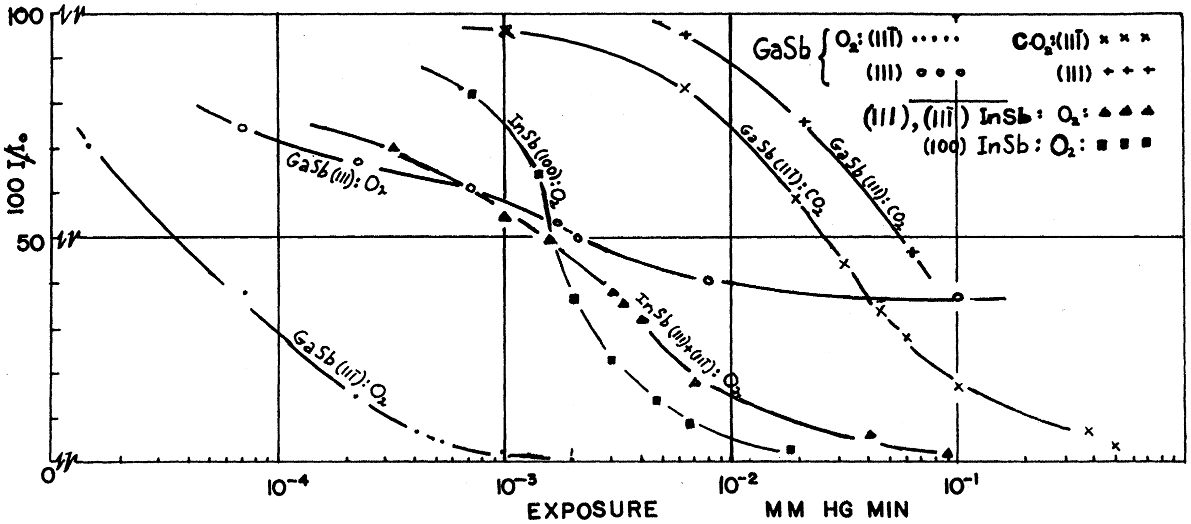

FIG. 3. Relative diffraction beam current (100 I/I_0) versus exposure to oxygen and carbon dioxide for (111) and (11$\bar{1}$) surfaces of GaSb and InSb, and (001) surface of InSb. Results for InSb [(111) and (11$\bar{1}$)] are from reference 2. Currents refer to integral-order beams only for carbon dioxide.

VI. REGENERATION AND SECONDARY EMISSION MEASUREMENTS

It was found that the oxygen-covered surfaces could be cleaned by heat treatment alone. For the GaSb, after light exposures corresponding to a fraction of a monolayer coverage (i.e., fractional decrease in beam intensities) the clean surface could be regenerated by heating to 350–400°C for periods of 10–20 minutes. After higher exposures, corresponding to more coverage, appreciably longer heating times were required to restore the clean surface. This correspondence between regeneration heating time and oxygen exposures (coverage) was noted even for exposures greater than those required to obliterate the diffraction patterns. This suggested that oxygen continued to adsorb on the surfaces even after coverages sufficient to obliterate the diffraction patterns, longer heating times being required to remove the greater quantities of oxygen.

These phenomena were checked by measuring the secondary electron emission of the surfaces as a function of oxygen exposure. The collimated beam of electrons used for diffraction measurements served as the primary beam, the total secondary electron emission being collected by the drum which surrounded the crystal and which was held at the same potential. Typical results are shown in Fig. 4. It is seen that the secondary emission for all surfaces continued to rise with oxygen exposure long after the diffraction pattern was obliterated. These results, which will be discussed below, are considered to show both that multilayer adsorption takes place and that a diffusion mechanism plays an important part in the removal of oxygen by heat treatment.

VII. CARBON DIOXIDE ADSORPTION CHARACTERISTICS

Carbon dioxide adsorption had not been studied in previous low-energy electron diffraction experiments on other materials since there appeared to be no special interest in its adsorption behavior. However, it was discovered, following an accidental exposure to this gas, that it adsorbed on GaSb so as to show lattice structure. Controlled experiments were then carried out. The high-purity gas was obtained from a Linde "M.S.C." source. Unlike other gases, it was admitted into the experimental tube without passing through a liquid nitrogen trap (to prevent freezing) but only through dry ice traps and in the presence of a molybdenum getter.

Adsorption of carbon dioxide on GaSb resulted in a weakening of all diffraction beams. As in the case of oxygen, the $(11\bar{1})$ face showed appreciably faster adsorption than the (111) face. Unlike oxygen however, it was found that the half-integral-order beams were weakened more rapidly than the integral-order beams. After sufficient adsorption the weak remaining pattern

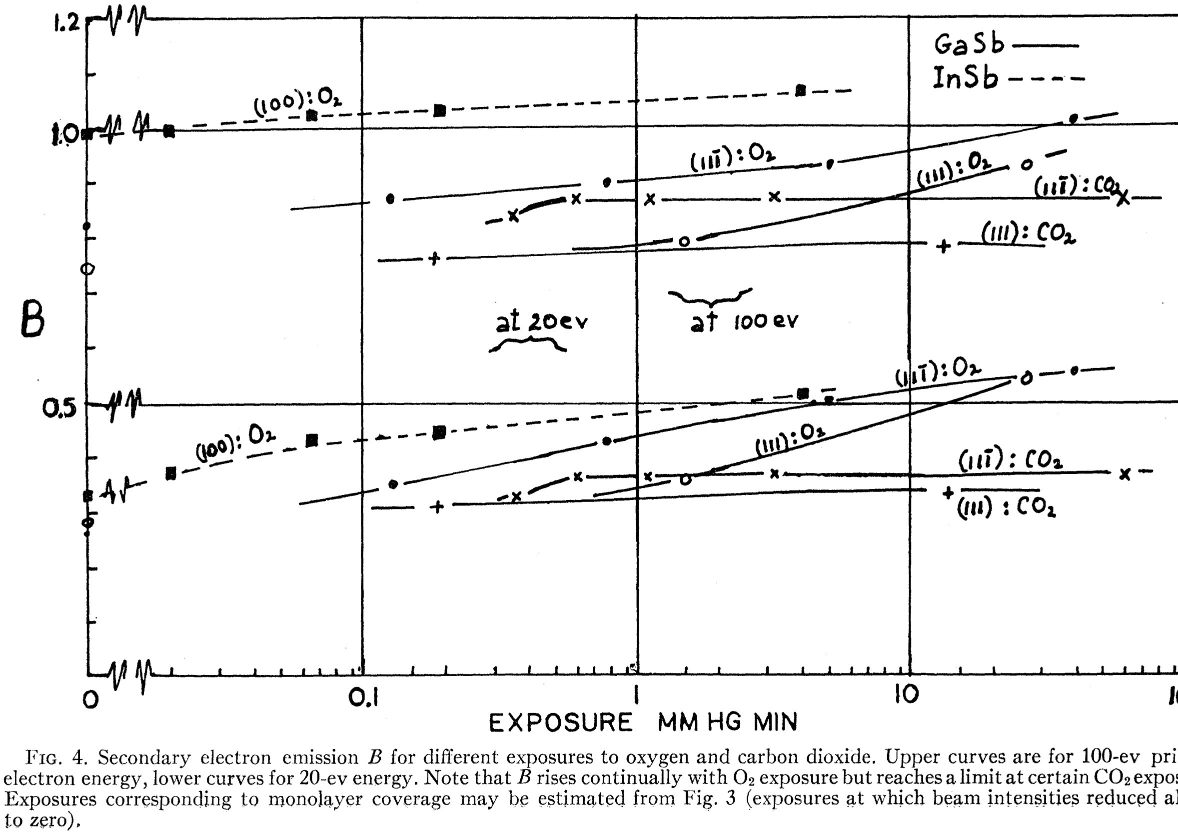

FIG. 4. Secondary electron emission B for different exposures to oxygen and carbon dioxide. Upper curves are for 100-ev primary electron energy, lower curves for 20-ev energy. Note that B rises continually with O_2 exposure but reaches a limit at certain CO_2 exposures. Exposures corresponding to monolayer coverage may be estimated from Fig. 3 (exposures at which beam intensities reduced almost to zero).

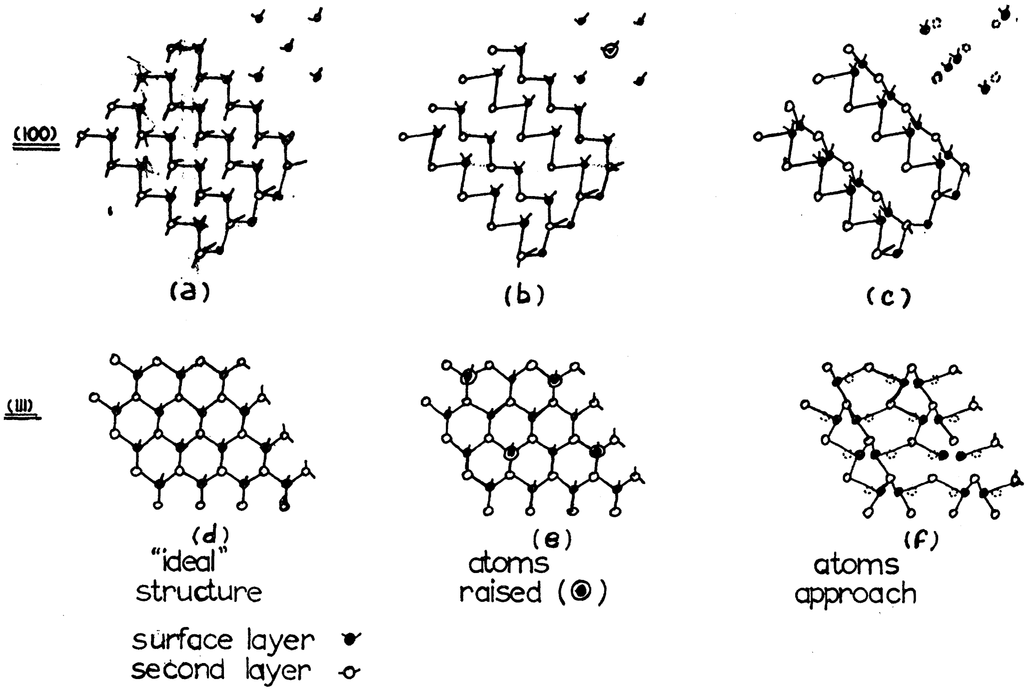

FIG. 5. Possible surface configurations for (111) and (100) surfaces of diamond-structure semiconductors. (100) surface viewed at oblique incidence, (111) surface at normal incidence. Probable distortions in second atomic layer when some surface atoms are raised, are not illustrated in this diagram. (a) "Ideal" (100) surface; (b) atoms in every second row of (100) surface raised with respect to neighboring rows; (c) (100) surface atoms approach in pairs (Schlier and Farnsworth[9]); (d) "ideal" (111) surface; (e) every second atom (counting along alternate close-spaced rows) raised with respect to its neighbors; (f) (111) surface atoms approach in pairs. Configurations (b), (c), (e), and (f) would lead to the observation of half-order diffraction beams. For (111) surface, configuration (e) is considered probable, see Fig. 6.

had only integral-order beams. A typical recorder trace after carbon dioxide adsorption is shown in Fig. 2(c).

Secondary emission measurements were made as a function of carbon dioxide adsorption. As for oxygen, the emission rose with exposure to carbon dioxide but reached a limiting value at the same exposures at which a very weak limiting diffraction pattern was attained. Higher exposures did not affect either the weak diffraction pattern or the secondary emission. Characteristics are shown in Fig. 4. It appears that multilayer adsorption of CO_2 does not take place.

Regeneration of the clean surface after CO_2 adsorption could not be achieved by heating up to 400–450°C. Higher temperatures were not used to avoid possible surface decomposition. After heating at 400–450°C for several hours the original diffraction pattern was partly restored. However, many beams were weak and broadened, with small extra beams present. Further, the secondary emission of such surfaces was significantly higher (3–5%) than for a surface cleaned by bombardment and annealing, indicating also that the heated surface was not equivalent to a clean surface. Apparently on heating, chemical reaction between the surface atoms and CO_2 takes place so as to retain the latter or its components in some form on the surface.

For the InSb, no significant change in diffraction beam intensities was observed even after CO_2 exposures of 1 mm Hg min, indicating negligible adsorption of this gas at room temperature. Tests with carbon monoxide indicated no significant adsorption of this gas on GaSb or InSb.

VIII. DISCUSSION

A. Structure of Clean (111) Surfaces

The occurrence of half-integral-order diffraction beams in the (110) and (112) azimuths is noteworthy. This feature has now been found for ion-bombardment cleaned (111) faces of Ge, Si,[1] InSb,[2] and GaSb, all of which are diamond-structure semiconductors. It was not found for (0001) faces of Bi_2Te_3,[6] which has a hexagonal structure. Diffraction patterns with half-order beams can be obtained from any surface atom configuration having a regularity with double the spacing of atoms in bulk (111) planes, e.g. Fig. 5(f). However, only one such configuration can lead to half-order beams having intensities comparable to those of integral-order beams, as had been found[2] for (111) and $(11\bar{1})$ surfaces of InSb. In this configuration, illustrated in Fig. 5(e), every second atom, counting along alternate close-spaced rows, is raised with respect to its neighbors, so that the actual surface layer consists of atoms whose spacing is exactly twice that of atoms in bulk (111) planes.

It is possible to give a general explanation for the

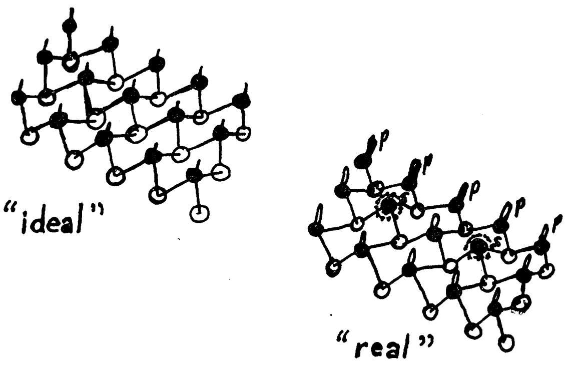

FIG. 6. (111) surface viewed at oblique incidence. Configuration labelled "real" shows every second atom (counting along close-spaced rows) raised with respect to neighboring atoms. Each raised atom has an *s*-type "dangling bond", with three *p*-type bonds to the sublayer. Remaining surface atoms have "dangling" *p* bonds and trigonal sp^2-type bonds to atoms in sublayer. Ratio of *s* bonds to *p* bonds, averaged over all surface atoms, is same in "ideal" and "real" configurations.

occurrence of such a structure on (111) surfaces of diamond-structure semiconductors.

On a "normal" (111) surface, prior to any rearrangement, each atom is bonded to three atoms in the second layer by tetrahedral sp^3 bonds. The fourth sp^3 bond is "dangling" perpendicular to the surface. Since its environment is now different from that in the bulk it is reasonable to suppose that the quantum state of this bond is altered. It may become either more *s* type or more *p* type. Of these two possibilities the latter would result in the electron staying mainly on the "outside", away from the other bonds, which appears reasonable. It is then proposed that the dangling bond tends to become *p* type. This would result in the remaining three bonds tending to become of type sp^2, instead of the former sp^3. Such trigonal bonds tend to be in a plane. Hence each surface atom will tend to be pulled down between the atoms in the second layer, exerting strong resultant lateral forces on these atoms. These pressures can be most easily relieved if the central atom within each hexagonal ring of atoms on the surface is forced up, as shown in Figs. 5(e) and 6. This would cause a reduction in the angular separation of the three filled bonds of the raised atom and could readily take place if one assumes that these three bonds become *p* type, having in consequence a natural angular separation of only 90°, instead of the former tetrahedral angle of 109°. Then the "dangling bond" of each raised atom will be *s* type, and the whole configuration would have a minimum strain, since the raising of the atoms shown in Fig. 6 allows the atoms in the former second layer to move laterally so as to relieve the pressure from the sp^2-bonded atoms. That is, every second atom, counting along any close-spaced row, is raised with respect to its neighbors. Three quarters of the original surface atoms have dangling *p* bonds and the remaining fourth, which are raised, have dangling *s* bonds. It is noted that this structure, which would account for the electron diffraction results, follows naturally as a result of assuming that the original dangling bond of a surface atom tends to become *p* type, rather than retaining an sp^3 type state, characteristic only of bulk bonding.

There are several consequences of this proposed structure of a clean (111) surface. Firstly, the amount by which every second atom is raised will depend on the strength of bonding between the atoms. If the bonding is very strong, the atoms will be able to move very little from their bulk positions. The raising of atoms relative to their neighbors will be small and the half-order diffraction beams weak. Conversely if the bonding is weaker, relatively greater raising is possible, perhaps of the order of 1 A, with stronger half-order beams resulting. In InSb the strength of bonding is significantly less than for Ge, Si, and GaSb (e.g., the forbidden energy gaps are, respectively, 0.25 ev, 0.75 ev, 1.1 ev, and 0.71 ev). Hence the half-order beams should be strongest for InSb, as was indeed found. The author has reported[2] that for (111) and (11$\bar{1}$) surfaces of InSb the half-order beams had intensities comparable with integral-order beams whereas for Ge, Si,[1] and GaSb the half-order beams were found to have intensities which were on the average only a quarter of the intensities of the integral-order beams. These observations are thus consistent with the model.

A second consequence is that the asymmetry of the zinc-blende structure (diamond-structure with alternate atoms different) in the [111] direction will be preserved when two faces [called (111) and (11$\bar{1}$)] are created by a cut parallel to (111) planes. Thus the (11$\bar{1}$) face would still consist of Group III atoms and the (111) face of Group V atoms. Before rearrangement a surface Group III atom would have a "dangling bond" containing $\frac{3}{4}$ of an electronic charge and a surface Group V atom would have a "dangling bond" with 5/4 of an electronic charge. These differences would not fundamentally affect the tendency for every second atom to be raised with respect to its neighbors but might affect the adsorption rates for gases on the two surfaces.

B. Adsorption Rates of Oxygen and Carbon Dioxide

As described in Sec. 5, the adsorption rates of oxygen and CO_2 on the Ga face of GaSb were about 10 times greater than on the Sb face. This is in contrast to InSb, where the adsorption rates of oxygen on the In and Sb faces were comparable. It now appears that the latter observation was simply due to the comparable activities of the In and Sb (111) faces of InSb. It is interesting to note that the oxygen adsorption rates on the Sb face of GaSb were similar, up to about half coverage, to those on the Sb face of InSb. See Fig. 3. Such a correspondence is expected since the faces are both composed of Sb atoms. At higher coverages the adsorption rates on the two surfaces diverge due to the influence of the different interiors of the two crystal surfaces.

The observed higher chemical reactivity[8] of "real" (111) faces than $(11\bar{1})$ faces is probably a complex phenomenon since these faces already have oxide layers. The interpretation of this on the basis of the above results, where the clean $(11\bar{1})$ or Ga face is initially more reactive, is that after the oxygen film is formed it would be held more tightly than that on the (111), or Sb, face leading to the observed lower reactivity for the "real" $(11\bar{1})$ face. The detailed mechanism however probably involves many processes.

As described in Sec. 7, the effect of adsorption of carbon dioxide on the GaSb faces was to cause the half-order beams to weaken faster than the integral-order beams. Assuming that the adsorbed particles were contributing to the diffraction pattern, this indicates that in the adsorbed layer the particles had spacings the same as those of atoms in bulk (111) planes of GaSb. If the CO_2 molecules dissociated on adsorption, the first step would be likely to be $2CO_2 \rightarrow 2CO + O_2$. One would then expect the CO molecules to desorb, since negligible adsorption of CO on clean surfaces was observed. This would leave only oxygen on the surface, yet an oxygen-covered surface showed no structure. Furthermore the CO_2-covered surface could not be regenerated by heat treatment up to 400–450°C whereas the oxygen-covered surface could be regenerated by heating to 350–400°C. From this evidence it is concluded that CO_2 adsorbed as an unbroken molecule, the linear molecules probably lying on the surface over definite sites, leading to the observed structure in the adsorbed layer. Apparently higher layers do not form at room temperature since the secondary emission did not change after exposures greater than those required to almost extinguish the diffraction patterns.

C. Secondary Emission and Regeneration Phenomena

We consider now the fact that the secondary emission of the oxygen-covered surfaces continued to rise with exposure after the diffraction patterns had been obliterated. It appears that the oxygen adsorbs initially either in an amorphous film or, possibly, in a polycrystalline monolayer arrangement. This causes the net diffraction pattern to weaken and disappear. The secondary electron emission arising from a monolayer itself is presumed to be very small, except at very low voltages, compared to the emission from the bulk where most of the incident electrons make collisions. Hence the observed rise in the secondary emission ratio B with gas coverage is mainly due to the effect of the adsorbed layer on the potential at the surface, apparently increasing the escape probability of internally created secondaries. Oxygen continues to deposit over the initial monolayer, causing further increase in B. The number of adsorbed layers can be estimated roughly from these data as about 3, assuming one monolayer nearly extinguishes the diffraction pattern and that B rises approximately linearly with depth of coverage.

If the adsorbed oxygen was simply desorbed when the surface was heated, one would expect that the second and third layers, being more loosely bound than the first, would desorb more easily than the first. Thus a given heat treatment which suffices to remove the first adsorbed layer should readily remove also the outer layers. However, it was observed for the InSb and GaSb surfaces that longer heating times (at a given temperature) were required to remove several layers of adsorbed oxygen than to remove approximately one layer. This suggests that a diffusion mechanism is operative in removing the oxygen during heat treatment, rather than simple desorption. This observation supports the proposal of Farnsworth[9] (for the case of Ge) that an important mechanism for the regeneration of clean surfaces by relatively low-temperatures heat treatment is diffusion of the adsorbed oxygen into the bulk of the crystal.

D. Structure of (100) Surfaces

The (100) surface diffraction patterns differ from (111) and (110) surface patterns, in that half-order beams are observed only in (110) and (310) azimuths and not in (100) azimuths. Such patterns were found by Schlier and Farnsworth[1] on (100) surfaces of Ge and Si, and have now been found also on (100) surfaces of InSb although in this case the patterns were generally weaker than for other surfaces. Schlier and Farnsworth[9] proposed a structure for a (100) surface which would lead to the above diffraction pattern being observed. This structure is formed by the surface atoms, which would normally have two dangling bonds, being pulled together in pairs, as shown in Fig. 5(c), in the direction of their dangling bonds. A possible alternative structure which is suggested by the model for the (111) surface, is one in which the atoms in every second row in the [110] direction are raised with respect to their neighbors. This is illustrated in Fig. 5(b). No detailed explanation of the bond characters in either model is presently available.

IX. CONCLUSION

The main results contained in this paper are:

(a) Observed half-order diffraction beams on clean (111) surfaces of diamond-structure semiconductors appear to be satisfactorily accounted for by the following model: Every second atom, (starting at a given atom and counting along any close-spaced row) is raised with respect to its neighbors. Each raised atom has a dangling s-type bond and three p-type bonds to the underlying atoms while the remaining three quarters of the surface

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[8] H. E. Gatos and M. C. Lavine, J. Electrochem. Soc. **107**, 427 (1960).

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atoms have each a dangling p-type bond and three trigonal sp^2-type bonds to the underlying atoms.

(b) The clean (111) and $(11\bar{1})$ surfaces of GaSb have different sticking coefficients for gases, the maximum values being 10^{-5} and 10^{-4} for oxygen on the Sb and Ga faces, respectively, and 10^{-6} and 10^{-5} for CO_2, respectively, these values being obtained by the method discussed in reference 2.

(c) Oxygen adsorbs in several layers at room temperature on (111) and $(11\bar{1})$ surfaces of GaSb and on (100) surfaces of InSb.

(d) The above clean surfaces may be regenerated by heat treatment alone after oxygen adsorption. An important mechanism for oxygen removal during heating to 350–400°C is diffusion into the bulk of the crystal.

X. ACKNOWLEDGMENTS

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Optical Constants of Silver

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The optical constants for electrolytically polished silver samples were determined from normal-incidence reflectance data in the spectral region 2 to 10 ev. The sharp minimum in the curve for k near 3.8 ev, which is associated with the onset of interband transitions, is deeper than in previous results. A second minimum is observed near 9.2 ev.

INTRODUCTION

The optical properties of metals have been the subject of many studies.[1] In the region of infrared frequencies, where free-electron absorption predominates, these processes may be described by the Drude equations. At higher energy, however, pronounced deviations from the Drude theory are observed in many cases. In the noble metals, this departure takes the form of a sharp minimum in the curve for k, the extinction coefficient. For silver this structure is particularly pronounced and much attention has been given to reflectance and transmission data in the vicinity of this absorption window.[2] Corresponding theoretical treatment, however, is less complete. There seems little doubt that this anomaly is associated with the onset of interband electronic transitions. The free-electron model, applied to silver with one electron per atom, would predict that the perfectly reflecting region should extend to the plasma frequency at about 9 ev.[3] Thus the free-electron model cannot be applicable to silver.

Recently, Suffczynski[4] has proposed a model which allows the calculation of the contribution of interband transitions to the optical constants of metals. For silver, the results are particularly interesting. The present investigation is a further study of the optical properties of this metal over an extended range of photon energy. The optical constants are determined in the region 2 to 10 ev by applying the Kramers-Kronig relations to normal incidence reflectance data.[5] The results are of especial interest because this range of energy includes the plasma resonance frequency calculated from the free-electron model.[3]

EXPERIMENTAL PROCEDURES

The techniques employed in these measurements have been described in a previous paper.[5] Reflectance data at 300°K for electrolytically polished[6] silver samples are shown in Fig. 1.[7] These values were obtained as soon as possible after the etching process and, although subject to conceivable atmospheric contamination, are considered a reasonable approximation to bulk silver reflectance characteristics.

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[1] For a review of this subject see M. P. Givens, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 6, p. 313; L. G. Schulz, Suppl. Phil. Mag. **6**, 102 (1957).

[2] For summaries of much of this work see R. S. Minor, Ann. phys. **10**, 581 (1903); L. G. Schulz, J. Opt. Soc. Am. **44**, 357 (1954); ibid., **44**, 540 (1954); L. G. Schulz and F. R. Tangherlini, J. Opt. Soc. Am. **44**, 362 (1954).

[3] D. Pines, Revs. Modern Phys. **28**, 184 (1956).

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[5] H. R. Philipp and E. A. Taft, Phys. Rev. **113**, 1002 (1959).

[6] L. I. Gilbertson and O. W. Fortner, Trans. Am. Electrochem. Soc. **81**, 199 (1942).

[7] The carefully measured reflectance data of Schulz (see work cited in footnote 2) are plotted below 3 ev. The measurements of Fig. 1 are fitted to his value at this point.