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FIELD EFFECT MEASUREMENTS ON THE ANODIZED SURFACES OF InSb

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Abstract: Field effect experiments have been performed at 77 °K on the real anodized surfaces ot p-type InSb. The surfaces of anodized specimens are very stable and have the surface charge Q_{SS} lower than usually. The surface potential u_{so} in the absence of electric field has been always positive indicating surface inversion. Discrete fast surface states were observed in the energy gap. The discrete state near the conduction band edge exibits density of about 3.10^{12} cm^{-2}, while the other groups of states are found to be less dense (6.10^{10} cm^{-2} — 9.10^{11} cm^{-2}). Some observation about field effect mobility and the occurence of prominent loops in the field effect patterns are discussed.

1. Introduction

In recent years there has been a number of investigations of the surface properties of the group III—V semiconductors that in general have similar bulk properties to Ge and Si. The primary emphasis was placed on the real InSb surfaces[1], and the field effect experiments have been performed on the A and B {111} »real« surfaces of InSb exposed to different ambients[2, 3, 4].

This paper is concerned with the surface properties of InSb. The experiments have been made with anodized p-type InSb at 77 °K. At liquid nitrogen temperature our material was p-type with conductivity of the order of 1 ohm^{-1} cm^{-1}. An anodizing process was used as a surface passivation technique. The electrical properties of anodized InSb surfaces are derived from large signal alternating field effect experiments at 77 °K. The density and energy distribution of surface states are deduced and some other phenomena are discussed.

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2. *Experimental*

Bulk electrical properties. Table 1 summarizes the bulk electrical properties of the InSb employed in the present experiments. The carrier concentration and mobility were determined by Hall effect and conductivity measurements. In all cases the mobilities measured at 77 °K were low,

Table 1.

Specimen	Carrier concentration (cm^{-3})	Conductivity (ohm^{-1} cm^{-1})	Hole mobility μ_{pb} (cm^2/V s)	Bulk potential u_b (kT)
No. 2	$8.6 \cdot 10^{15}$	1.32	980	—15
No. 3	$5.2 \cdot 10^{15}$	0.856	1030	—15
No. 4	$8.9 \cdot 10^{15}$	2.16	1510	—16
No. 5	$1.2 \cdot 10^{16}$	1.44	755	—16.1

indicating high compensation by donors. The effective mass values were taken from Hilsum and Rose-Innes[5] and energy gap ($\approx$ 40 kT) was determined from data by Hrostowski et al.[6]. The mobility ratio $b = \mu_{nb}/\mu_{pb}$ was taken 30. The bulk potential u_b was determined as usually employing the Hall coefficient and nondegenerate statistics.

The dimensionless potential u is defined by equation

$$u = \frac{E_F - E_i}{kT},$$

where E_F is Fermi level, and E_i the instrinsic Fermi level. The value of u in the bulk is called the bulk potential u_b, and its value at the surface the surface potential u_s.

Sample preparation and experimental technique. Single crystal specimen of InSb measuring $10 \times 3{,}5 \times 1$ mm^3 were mechanically polished. Contacts were made by soldering with indium using Zinc chloride flux. The sample was given a standard etch treatment in a diluted CP-4A etch. Then it was rinsed in deionized water to which a trace (10^{-6} molar) of Na_2S has been added, and anodized in 0,1 N KOH solution[7]. For a time of 5 min and a constant voltage source (220 V) an oxide layer was formed having thickness of several microns. At such a high rate of formation of the anodic films (greater than 4 V/s) no effect of crystal orientation is observed (Dewald[7]), and the surface charge is lower than usually (Chang and Howard[8]). The oxide layer protects the surface of uncontrolled contaminations. Etched surfaces without anodic films have the density of surface states so large (of the order of 10^{15} cm^{-2}, Davis[2]) that it is impossible to shift the surface conductivity sufficiently to determine their properties.

The field plate was finally clamped to the surface of the specimen with a melinex sheet (of 0,02 mm thickness) sandwiched in between. The whole system was immersed in liquid nitrogen and submitted to the field effect

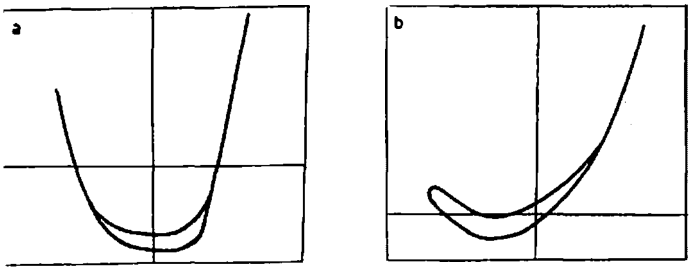

Fig. 1 — Field effect patterns as taken from the oscilloscope for
a) specimen No. 2 — a few hours after the preparation,
b) specimen No. 3 — just after the preparation.

experiment[9, 10]. The sinusoidal voltage was 3 kV peak to peak with frequency of 50 cps. Conductivity change due to the capacitively applied electric field was displayed on the vertical axis of an oscilloscope, against the signal proportional to the induced charge on the horizontal axis.

3. *Results and discussion*

Field effect patterns for two typical cases are represented in Fig. 1. The experimental curves of the change in the surface conductance $\Delta\sigma_S$ per square

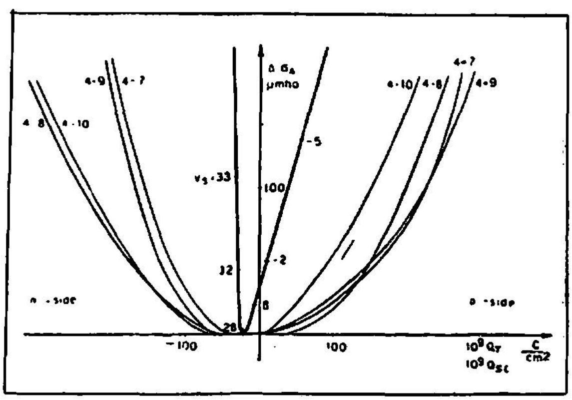

Fig. 2.
——— theoretical curve $\Delta\sigma_S (Q_{SC})$ for specimen No. 4.
——— experimental curves $\Delta\sigma_S (Q_T)$ for specimen No. 4,
which was etched and anodized. Curves 4—7, 4—8, 4—9 and 4—10 represent measurements taken the second, third, fifth and twentieth day respectively after the preparation of the specimen. The surface potential u_{s0} is about 11 kT. Indicated on the theoretical curves are the values of the potential barrier height v_s.

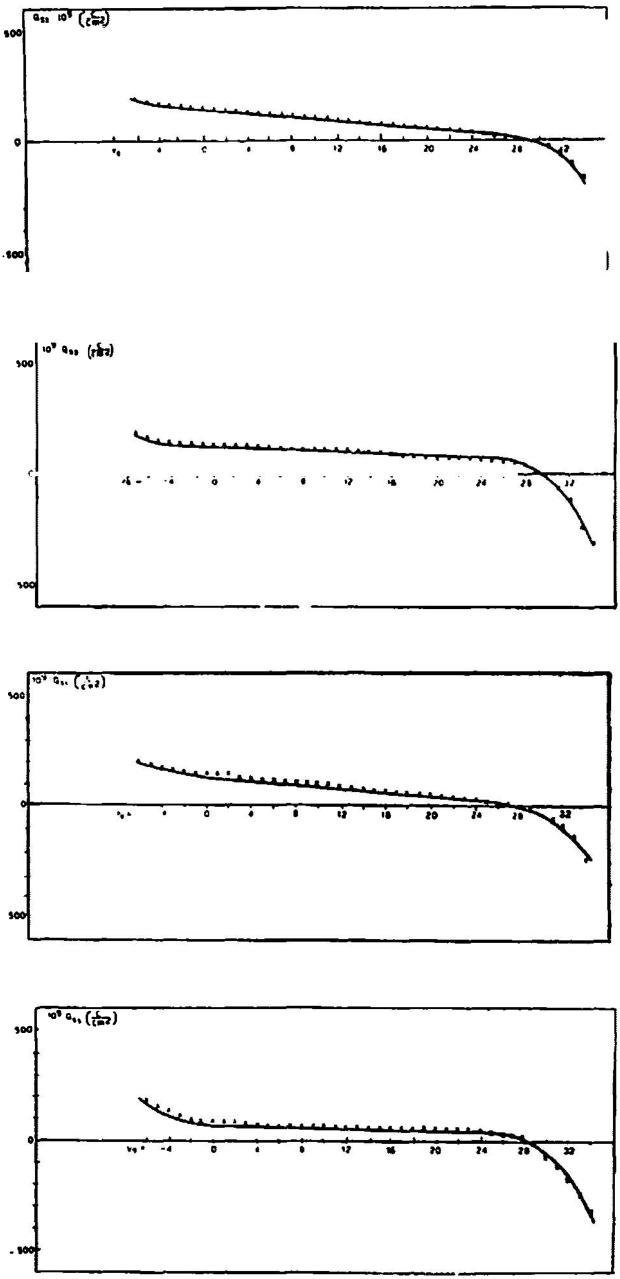

Fig. 3—6 — The change in trapped charge per cm^2 as a function of the surface barrier height v_s for specimen No. 4. Data were obtained from curves plotted on Fig. 2.

—— experimental curve: $Q^f_{ss} = Q_T - Q_{sc} - Q^s_{ss}$,

xxxxx theoretical curve: $Q_{ss} = -e \sum \frac{N_{tj}}{1 + \exp(u_{tj} - u_s)}$.

versus induced charge Q_T per cm^2 are shown on Fig. 2. The theoretical curve $\Delta\sigma_S$ versus space charge Q_{SC} corresponding to the absence of the surface states is also plotted and is based on the procedure of Kingston and Neustadter[11]. Schrieffer's[12] correction for the mobility of carriers near the surface was not taken into account. The total charge density Q_T induced at the semiconductor surface is distributed between the space charge region and the surface states. A part Q_{SS} is trapped in the surface states and is thus immobilized, and a part Q_{SC} may enter the space charge region of the semiconductor below the surface and is mobile contributing to the conductivity parallel to the surface. Thus, we may write

$$Q_T = Q_{SC} + Q_{SS}$$

For a given semiconductor and temperature Q_{SC} is a known function of the surface barrier height $v_s = u_s - u_b$, while the charge Q_T is known from the geometrical capacitance and applied voltage. So, following Brown's[13] procedure, we obtain from the data of Fig. 2 the change in the surface charge Q_{SS} per cm^2 versus the surface barrier height v_s, which is shown in Fig. 3—6. The charge Q_{SS} is equal to

$$Q_{SS} = Q^f{}_{SS} + Q^s{}_{SS},$$

where $Q^f{}_{SS}$ and $Q^s{}_{SS}$ is the charge in the fast and slow surface states, respectively. Fortunately, the use of AC fields as a means of varying the potential barrier and the long time constants (especially at low temperatures — hours) associated with slow states, makes it easy to eliminate their effect, leaving only the fast surface states as active participants in the charge trapping process.

The trapped charge Q_{SS} obeys Fermi-Dirac statistics and the occupation of the surface states of density N_{tj} and energy E_{tj} is given by

$$Q_{SS} = -e\sum_j \frac{N_{tj}}{1 + \exp(u_{tj} - u_s)}$$

where $u_{tj} = (E_{tj} - E_i)/kT$. It can be seen that Q_{SS} depends on the band bending at the surface. This then allows N_{tj} and u_{tj} to be deduced by curve fitting, but these parameters can only be obtained uniquely from the field effect measurement if the amount of the band bending is very large.

From series of experiments we may conclude that anodic layer on p-type InSb decreases the density of surface states. The positive surface charge makes the surface of p-type InSb inverted, which means that the surface potential u_{so} in the absence of electric field is positive. Some experimental data were taken just after the preparation of the anodic film, but most of the experiments were performed allowing just enough time to elapse after the formation of the anodic film. The units have not been heat-treated or exposed to different ambients. These data indicate that the anodized surface of InSb is very stable under normal room temperature conditions and we have noticed no changes (within the range of experimental error) in the characteristics of the surface states in a time interval from one hour to twenty days after preparation of the specimens.

Table 2.

The caracteristics of InSb surfaces. Energy positions of surface states are given in units kT relative to the intrinsic Fermi level. Densities are given in units $10^{12}cm^{-2}$

p-type	u_{t1}	N_{t1}	u_{t2}	N_{t2}	u_{t3}	N_{t3}	u_{t4}	N_{t4}	u_{t5}	N_{t5}	u_{t6}	N_{t6}
2V—1	15	1.25	7	0.313	—1	0.125	—7	0.125	—13	0.125	—21	0.313
2V—2	17	1.87	13	0.313	5	0.313	—3	0.313	— 9	0.62	—14	0.313
3A	17	3.13	9	0.313	0	0.187	—7	0.187	—13	0.187	—19	0.62
3B	18	3.13	10	0.062	3	0.062	—5	0.062	—13	0.062	—22	0.94
4—1	17	2.5	14	0.313	7	0.313	0	0.125	— 8	0.125	—20	0.62
4—2	18	3.13	12	0.313	4	0.313	—4	0.187	—12	0.187	—19	0.313
4—3	19	4.38	15	1.25	9	0.313	0	0.313	— 9	0.313	—19	0.313
4—4	18	4.38	11	0.313	3	0.125	—5	0.125	—13	0.125	—20	0.125
4—5	17	4.38	11	0.313	3	0.125	—5	0.125	—13	0.125	—20	0.125
4—6	18	4.38	12	0.62	4	0.125	—4	0.125	—12	0.125	—20	0.125
4—7	17	1.25	12	0.313	4	0.313	—3	0.125	—10	0.125	—19	0.125
4—8	17	3.3	11	0.313	4	0.125	—4	0.125	—12	0.125	—19	0.313
4—9	16	1.25	13	0.62	5	0.313	—4	0.313	—13	0.313	—19	0.313
4—10	17	2.5	12	0.62	4	0.06	—4	0.06	—10	0.06	—20	0.6
5A	18	3.13	14	0.94	5	0.62	—3	0.125	—10	0.125	—21	0.62
5C	16	2.5	8	3.13	1	0.25	—7	0.25	—14	0.313	—21	1.25

With anodized surfaces in the field effect experiment it is possible to scan a large interval of values of the surface barrier height (from $v_s = -6\,kT$ to $v_s = 32\,kT$) and the minimum of surface conductivity is always obtained. The results on the quantity of charge captured in the surface states as a function of the position of Fermi level at the surface may be interpreted with six groups of fast surface states. They are symmetrically distributed around the center of the energy gap in intervals of about 7 kT. The first group of these states located at about 4 kT below the conduction band edge has the density of approximately $3 \cdot 10^{12}$ cm^{-2}. The other groups of states which could be resolved in these experiments have a lower density than the first one (between $6 \cdot 10^{10}$ cm^{-2} and $9 \cdot 10^{11}$ cm^{-2}). The results are given in Table 2. The MOS capacitance measurements at 77 °K (Chang and Howard[8] and Chang[14]) on the anodized p-type InSb provide the same information: the surface is inverted and the surface charge is positive with density of the order of 10^{11} cm^{-2}. In the field effect experiment on the A and B {111} surfaces of InSb in different ambients by Kawaji[3] and Huff, Kawaji and Gatos[4] discrete fast surface states were observed in the energy gap with densities between 10^{11} cm^{-2} and 10^{12} cm^{-2}. We have not been able to investigate the effect of the anodic oxide on the surfaces of exactly determined orientation, but we believe that our results make possible the use of the anodic oxide in the surface controlled experiments.

The slope of the curves $d\Delta\sigma_S/dQ_T$ on Fig. 2 gives the field effect mobility $\mu_{f\text{-}eff}$. On the n-side of conductivity curve $\mu_{f.eff.}$ is lower than the bulk mobility μ_{nb}, because for v_s of about 3 kT Fermi level passes through the surface states of large density. At the same time the electrons move here in a deep inversion layer, where their mobility is lowered due to additional scattering on the walls of a potential well. It should be pointed out at the same time, that for large values of $\Delta\sigma_S$ experimental curve is steeper on the p-side as compared with slope of the theoretical curve $\Delta\sigma_S\,(Q_{SC})$. This means that the field effect mobility of holes is higher than the bulk mobility. This experimental result can be explained by noticing that these points of the experimental curve correspond to the values of the barrier height v_s below $-5\,kT$. This is the case of a deep accumulation layer, where the Fermi level enters the valence band and therefore for the calculation of theoretical curves $\Delta\sigma_S\,(Q_{SC})$ degenerate statistics must be used. The results of Davis[2] also show that the field effect mobility is approximately equal to the bulk hole mobility. He concluded that the scattering mechanism in the surface layer do not affect the hole and electron mobilities in the same way. This point has not been clarified so far.

In all field effect patterns on Fig. 1 the loops occur on the side of the pattern corresponding to minority and majority carrier conduction. The loops at low temperatures were observed by Montgomery and Brown[15] on p- and n-type Ge, but always on the side corresponding to minority carrier conduction. We suppose that in this case the observed phenomenon is a consequence of unbalanced generation-recombination processes, when minority carriers cannot be supplied through ohmic contacts at the end of the specimen. On the side corresponding to majority carrier conduction any charge exhange takes place exclusively between the surface states and the majority carrier band so that final equilibrium conditions are reached with relaxation times proportional to exp $[(E_v - E_t)/kT]$. These relaxation times may be very large at low temperatures and for surface states far from valence band edge E_v. Through experimental investigation of such processes considerable light could be shed on the characteristics of the surface states involved.

4. Conclusions

As far as available literature has been consulted these are the first field effect measurements done on the anodized surfaces of InSb.

From the experiments that have been described, we can make a few statements about the fast surface states that exist on anodized InSb surface. The density of these states are lower on anodized than on etched surfaces. The positive charge trapped in them makes the surfaces of p-type InSb inverted. The fast surface states are at least approximately unchanged under normal room conditions. The dependence of the charge trapped in the surface states as a function of position of the Fermi level in the band gap, indicates that in the forbidden gap there are six groups of fast surface states. The first group below the conduction band edge has the density of $3 \cdot 10^{12}$ cm^{-2}, but the other groups of states have lower density ($6 \cdot 10^{10}$ cm^{-2} — $9 \cdot 10^{11}$ cm^{-2}). These results are in agreement with those obtained from capacitance measurements[8, 14] on anodized surfaces of InSb.

Since the time constants of the slow and fast states are orders of magnitude apart, slow states are inoperative at this frequency, and we can deliberately exclude them in the charge trapping process.

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MJERENJA EFEKTA POLJA NA ANODIZIRANIM POVRŠINAMA In Sb

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Sadržaj

Vršena su mjerenja efekta polja na realnim površinama indium antimonida kod temperature tekućeg dušika. Površine primjeraka bile su obrađene standardnim postupcima brušenja, poliranja i kemijskog jetkanja, a zatim su bile podvrgnute anodizaciji u 0,1 N KOH otopini. Površine ovako obrađenih primjeraka imaju smanjenu gustoću površinskih stanja, stabilne su i omogućuju da se modulacija vodljivosti pomoću efekta polja ostvari u širokom intervalu vrijednosti površinskog potencijala. Korišten je efekt polja velike amplitude kod frekvencije od 50 Hz.

Dobiveni rezultati o količini zahvaćenog naboja u zavisnosti od položaja Fermi nivoa na površini mogu se interpretirati pomoću šest grupa brzih površinskih stanja simetrično raspoređenih s obzirom na sredinu zabranjene zone u razmacima od oko 7 kT. Prva grupa, uz rub vodljive vrpce, ima gustoću reda veličine 10^{12} cm^{-2}, dok ostale grupe imaju gustoću za jedan do dva reda veličine manju. Diskustirana su neka zapažanja o pokretljivosti efekta polja i pojavi prominentnih petlji na krivuljama osciloskopa.