

# Surface states of lead selenide crystals

D. V. Kazantsev, Yu. G. Selivanov, V. T. Trofimov, and E. G. Chizhevskii  
*P. N. Lebedev Physics Institute, Russian Academy of Sciences, 117924 Moscow, Russia*

(Submitted 25 July 1995)

*Pis'ma Zh. Éksp. Teor. Fiz.* **62**, No. 5, 422–426 (10 September 1995)

An image of a section of a surface on a (100) cleavage surface of a PbSe single crystal, grown by the free-growth method, was obtained with atomic resolution by the method of scanning tunneling microscopy in the tunneling current stabilization regime. The density of states, measured near the band edges, indicates that the Fermi level is pinned on the surface of the crystal. © 1995 American Institute of Physics.

## FORMULATION OF THE PROBLEM

Difficulties arise in the measurement of the spectrum of surface states of narrow band gap semiconductors, since the accuracy of standard methods (for example, ultraviolet photoelectron spectroscopy) is comparable to the band gap  $E_g$ , which for PbSe is equal to only 264 meV at  $T=300$  K. The position of the Fermi level at the surface of IV–VI semiconductors has been studied in Ref. 1 only for PbS, where it was determined that for  $n$ - and  $p$ -type crystals a region which is depleted of majority carriers is formed near the surface. For the narrower-bandgap compound PbSe it was concluded from an analysis of the Hall data for epitaxial layers of thickness 0.05–1  $\mu\text{m}$  and from the dependence of the resistance on the holding time in air that a surface layer with a thickness of up to 1  $\mu\text{m}$  and strong (more than  $10^{18} \text{ cm}^{-3}$ )  $p$ -type conductivity is present, irrespective of the type of conductivity in the bulk of the material.<sup>2,3</sup> This is associated with the doping action of oxygen, which is an acceptor for VI–VI semiconductors. However, the position of the Fermi level at distances of the order of the Debye length from the surface was not studied. In Ref. 4 it was concluded by an indirect method from an analysis of the characteristic features of the decay of the photoconductivity signal for thin ( $< 1000 \text{ \AA}$ ) epitaxial layers of PbSe that there exists a pair consisting of acceptor and donor surface states which at liquid-helium temperatures lie near the center of the band gap. As a result of the trapping of the majority carriers in these levels, a depletion region is formed near the surface in  $n$ - and  $p$ -type epitaxial layers. In the present work we measured by a direct method the position of the Fermi level on a PbSe surface and we concluded that it is pinned by the surface states.

## EXPERIMENTAL PROCEDURE

We measured the spectrum of surface states by analyzing the first derivatives of the  $I-V$  curves that correspond to the energy density of the states (tunneling-spectroscopy method). The measurements were performed on freshly cleaved surfaces of  $n$ - and  $p$ -type PbSe single crystals, grown by the free-growth method, with a carrier density of  $(0.5-5) \times 10^{18} \text{ cm}^{-3}$ . The dislocation density on the cleavage surface of a crystal did not

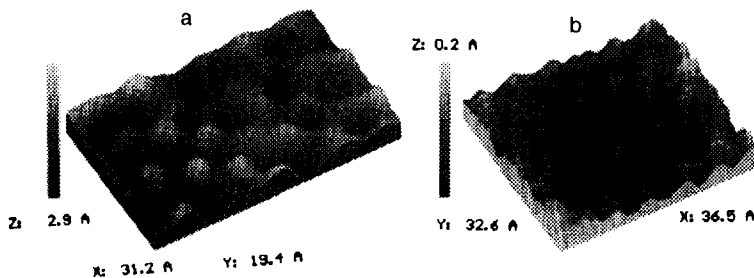


FIG. 1. Image of the cleavage surface of *n*-PbSe (a) and *p*-PbSe (b). The tip voltage is 48 mV and the current is equal to 0.9 nA. The scanning rate is equal to 500 Å/s. A  $5 \times 5$  linear filtering matrix, whose size corresponds to 0.8 Å on the surface, with a central rate of 10 was used to smooth the images.

exceed  $10^4 \text{ cm}^{-2}$ . A SKAN-10 tunneling microscope with a Pt/Ir tip was used for the measurements. This microscope, built at the Moscow State University, has a sensitivity of  $\leq 0.1 \text{ \AA}$  along the normal to the surface and a positioning accuracy of  $\leq 0.2 \text{ \AA}$  with a  $0.6\text{-}\mu\text{m}$  scanning field. The derivatives of the current-voltage characteristics were measured by a modulation method at a frequency of 5 kHz using a lock-in technique; the modulation amplitude was  $\sim 10 \text{ mV}$ . The measurements were performed at a temperature of 300 K without evacuating the microscope.

## EXPERIMENTAL RESULTS

An image of a section of the cleavage surface of an *n*-PbSe crystal is shown in Fig. 1a; a similar image for a *p*-type sample is shown in Fig. 1b. The tip voltage is 48 mV (grounded sample) and the tunneling current is 0.9 nA. A periodic structure exhibiting short- and long-range order is observed. The period of the square lattice is  $4.3 \text{ \AA}$ , which agrees well with the period of the face-centered lattice of a bulk crystal of lead selenide, equal to  $6.126 \text{ \AA}$ , divided by  $\sqrt{2}$ . High-quality images of the surface were obtained by exposing the cleaved surface to air for not more than 1 h for *n*-type crystals and not more than 3 h for *p*-type crystals. The images shown in Fig. 1 were obtained after several tens of scannings over the selected section, which is probably attributable to the gradual removal of adsorbed atoms and oxides from the surface of the crystal.

For measurements of the differential conductivity, the tunneling tip was brought up to a selected point on the surface with a current of  $\approx 0.6 \text{ nA}$ , after which the feedback was cut off (the tip was frozen). The drift of the tip during the measurements did not exceed  $1 \text{ \AA}$ .

Figure 2 shows the differential conductivity as a function of the applied bias voltage. The curves were measured at different points of the surface after a scanning image of the crystal was obtained. The branches for the positive and negative bias voltages correspond to states below and above the Fermi level, respectively. The width of the region of low differential conductivity between the cutoff voltages approximately corresponds to the band gap in PbSe. The  $I-V$  curve for *p*-PbSe crystals is shifted into the negative bias region and is virtually structureless. For the *n*-PbSe crystal the cutoff voltage on the positive-voltage side is  $\sim 120 \text{ meV}$ , and a well-reproducible structure consisting of sev-

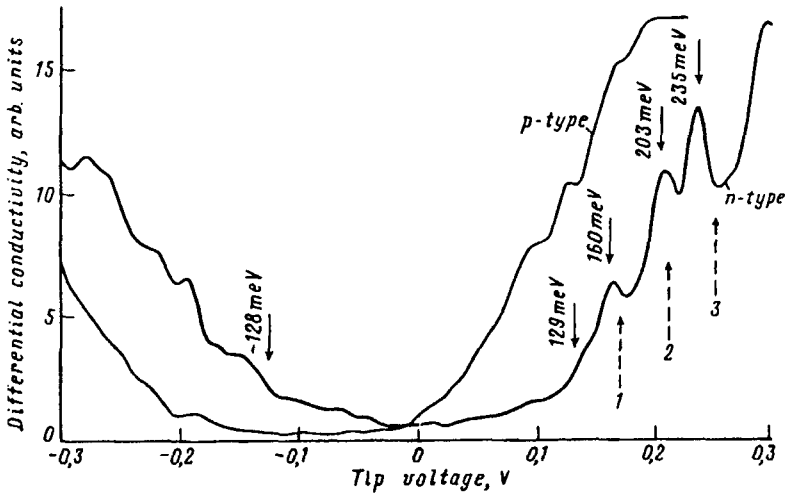


FIG. 2. Differential conductivity of *n*-PbSe and *p*-PbSe as a function of the voltage on the tunneling gap for the samples shown in Fig. 1.

eral peaks is observed on the right-hand branch of the  $I-V$  curve. Extrema are observed irrespective of the choice of the measurement point, but their position and amplitude vary slightly. The structure of the spikes on the left-hand branch of the  $I-V$  curve is poorly reproduced and the amplitude of the spikes is comparable to the measurement error.

## DISCUSSION

The fact that a high-quality image of the PbSe surface, whose lattice symmetry and lattice constant correspond to their values in the bulk of the crystal, is observed for several hours after cleavage indicates that the surface is not subjected to oxidation erosion during the measurements. Scanning of the tip above the surface apparently causes a partial removal of adsorbed atoms and a part of the oxide layer.

The curves of the differential conductivity versus the bias voltage are explained by carrier tunneling in the region of band bending produced near the surface by the charged surface states. Since for a narrow band gap semiconductor at  $T=300$  K the resistance of the tunneling gap is several orders of magnitude higher than the resistance of the depletion layer, it can be assumed that the total voltage drop occurs across the tunneling gap. In this case the differential conductivity is proportional to the electronic density of states in the bands.

The cutoff voltage for which the tunneling current increases sharply is equal to the splitting between the Fermi level at the surface of the crystal and the band edge. Therefore, in *n*-type crystals with carrier density varying over wide limits  $(0.5-5) \times 10^{18} \text{ cm}^{-3}$ , the Fermi level at the surface of the crystal lies 140–180 meV below the edge of the conduction band. In the bulk with  $n=5 \times 10^{18} \text{ cm}^{-3}$  the Fermi level lies 31 meV above the edge of the conduction band; i.e., the Fermi level is pinned at the surface. This happens in the case where the surface state lying  $\sim 144$  meV below the conduction band

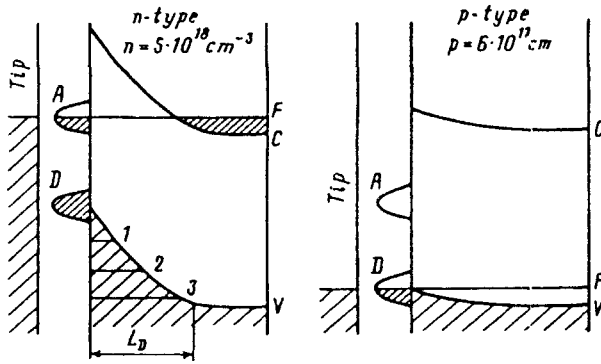


FIG. 3. Energy-level diagram of a tunneling contact with *n*-PbSe (a) and *p*-PbSe (b).

is of an acceptor character. The small change in the position of the pinned Fermi level is apparently associated with the large width of the surface state (caused, for example, by inhomogeneous broadening of the state). Figure 3a shows an energy-level diagram of a tunneling contact for *n*-PbSe with  $n = 5 \times 10^{18} \text{ cm}^{-3}$ . The quantum well arising as a result of the band bending in this case is  $\sim 270 \text{ \AA}$  wide and  $\sim 166 \text{ meV}$  deep. The computed position of the quantum-size levels in a triangular well, whose parameters have the values indicated above, is shown in Fig. 3. The position of the quantum-size levels agrees well with the peaks in the differential conductivity (dashed lines in Fig. 2). The spike structure on the right-hand branch of the differential conductivity of *n*-PbSe is therefore associated with vertical tunneling (the tunneling electron has a momentum perpendicular to the surface of the crystal) on the quantum-size levels. The nature of the surface states is apparently associated with the defects of the surface structure, oxidation of some of the lead atoms, and the formation of uncompensated selenium bonds. As was shown in Ref. 4, the photoconduction signal due to the trapping of carriers in surface states increases as the surface oxidizes or selenium is deposited on it.

In *p*-type crystals the Fermi level is basically tied to the edge of the valence band, irrespective of the position of the Fermi level in the bulk which ranges from  $-30$  to  $30 \text{ meV}$  with respect to the edge of the valence band, depending on the carrier concentration in the volume of the semiconductor. This happens in the case where the surface state lying at the edge of the valence band is of a donor character. The band bending is small. As a result, the quantum well contains one shallow level and the differential conductivity as a function of the bias voltage is structureless.

The pinning of the Fermi level at the surface of the wide band gap semiconductors (for example, III-V) is a standard, well-known phenomenon.<sup>5,6</sup> It is explained by surface states which split off from the conduction band or valence band and, accordingly, are initially empty or filled. In narrow band gap IV-VI semiconductors, the average band gap over the Brillouin zone is greater than  $1 \text{ eV}$  and is small only at the *L* point. As a result, the levels of the deep impurity states and defects are usually superimposed on the band continuum. The only exceptions are  $\text{Pb}_{1-x}\text{Sn}_x\text{Te}(\text{In})$  ( $x \sim 0.25$ ) and  $\text{PbTe}(\text{Ga})$ , for which the level of one of the charge states lies in the band gap. Consequently, the pinning

of the Fermi level at the PbSe surface is by no means a standard phenomenon. Apparently, the tying of the Fermi level to the center of the band gap was also observed on the PbS surface.<sup>1</sup> Since the experimental data are limited, at present no conclusions can be drawn about whether or not the arrangement of the surface level in the band gap of lead selenide is accidental.

In summary, in the present study we obtained high-quality images of the surface of the narrow band gap semiconductor PbSe with atomic resolution in air at room temperature. The band bending at the surface was measured by a direct method. As a result, it was confirmed that the Fermi level is pinned at the PbSe surface. The position of the acceptor level agrees well with the level introduced in Ref. 4. The position of the donor level is substantially different. This difference could be attributed to temperature shift of the level itself and of the band edges.

We wish to thank B. A. Volkov for a discussion of the results. This work was supported by the Russian Fund for Fundamental Research (projects 94-02-05849-a and 93-02-17261).

<sup>1</sup>T. Grandke and M. Cardona, *Surf. Sci.* **92**, 385 (1980).

<sup>2</sup>J. D. Jensen and R. B. Schoolar, *J. Vac. Sci. Technol.* **13**, 920 (1976).

<sup>3</sup>K. Seetharama Bhat and V. Damodara Das, *Phys. Rev. B* **32**, 6713 (1985).

<sup>4</sup>V. T. Trofimov, Yu. G. Selivanov, and E. G. Chizhevskii, *Fiz. Tekh. Poluprovodn.* **30**, (1996) (in press).

<sup>5</sup>J. Tersoff, *J. Vac. Sci. Technol. B* **3**, 1157 (1985).

<sup>6</sup>W. Walukiewicz, *Phys. Rev. B* **37**, 4760 (1990).

Translated by M. E. Alferieff