V.S. Edel'man. The development of scanning tunneling microscopy. The development of the scanning microscopy started by the classical studies of G. Binnig and G. Rohrer is ever gaining in tempo. The circle of studies is expanding, the instrumental base is developing, and new ideas and methological procedures are appearing, and combinations of different methods are being mastered (see the review of Ref. 1). The most impressive results of the method are the obtaining of images of the surface with atomic resolution. At present such measurements have ceased to be unique and have entered into the broad practice of solid-state physics. The fundamental problem in performing such studies, if we are not speaking of especially inert materials such as pyrolytic graphite, is the cleaning of the surface and the maintenance of this state, which is usually attained by in situ treatment (cleavage, ion etching, annealing) in a high vacuum. Among the most interesting studies we note the observation of a GaAs-AlGaAs boundary in a cross section of a test structure containing alternating layers of GaAs and Al<sub>0.38</sub> Ga<sub>0.62</sub> As.<sup>2</sup> It was established that the transition from the one region to the other occurs within the bounds of one to two lattice constants. In studies under high-vacuum conditions of cleavage faces of previously deformed gallium arsenide with a density of dislocations  $\sim 10^8$  cm<sup>-2</sup>, it was possible to observe the emergence of dislocations to the surface.<sup>3</sup> The STM image showed that the crystal lattice changes very little even in the immediate vicinity of the core of a dislocation, while the dislocation itself is manifested in the fact that a step two atoms high starts from its core.

In a set of studies (see Ref. 4 and the references cited there), Avouris and his associates performed an elegant investigation of chemical reactions on an atomic scale, having supplemented their previous studies of the interaction of Si with NH<sub>3</sub> with the study of the reactions Si-O<sub>2</sub>, Si-N<sub>2</sub>O, Si-B<sub>10</sub>H<sub>14</sub> (decaborane), and Si-H<sub>2</sub>O, by investigating the reaction on the  $7 \times 7$  reconstructed surface of Si(111).

Currently the investigators working in the STM field are trying to expand the possibilities of the method by observing different nonlinear effects. We shall demonstrate the prospects opened up here with several characteristic examples.

1. STM under conditions of optical photoexcitation. Illumination of the region of a tunneling contact gives rise to a photovoltaic effect. This phenomenon was observed in Ref. 5. The photo-emf reflects the structure of the surface on an atomic scale, while defects strongly influence its magnitude. Thus, an oxygen atom adsorbed on the surface leads to a decline in the photo-emf in a region with dimensions  $\sim 2$  nm owing to increase in the rate of recombination of electronhole pairs. The acceleration of recombination is apparently caused by the breakdown of translational symmetry at the surface. 2. Emission of light from the tunneling gap. The first experiments to detect light emitted in inelastic tunneling in STM<sup>6</sup> showed that one must increase the light-gathering power for a systematic study of this effect. A rather simple method for increasing the solid angle  $\theta$  of light collection to a value  $\sim \pi$  was proposed in Ref. 7. In this study the stylus for the STM was created as follows. The outer layer was removed from the end of a fiber light guide, and a thin layer of metal (Ag, Au, Pt) was deposited on the freed quartz core of diameter  $\sim 100 \,\mu$ m. Then the quartz fiber was broken so that the end of the quartz was opened for receiving photons, while the metal coating about the perimeter could serve as the stylus of the STM. The other end of the light guide was introduced into a photomultiplier directly, or with a light filter placed between them.

With this photo-STM it was possible to receive radiation from surface plasmons and show that their spectrum depends on the material of both the specimen and the stylus. Figure 1 shows one of the spectra for the Au-Au pair. The



FIG. 1. Dependence of the emission intensity I on the voltage across the tunneling gap  $V_{\rm T}$  for the tunneling gap Au-Au (1) and for the case in which the Au specimen is covered with a monolayer of copper phthalocyanine (2-4). To measure the intensities in 3 and 4, a filter was set ahead of the photomultiplier with a transparency region near 1.8 or 3.6 eV, respectively (the transparency regions are shown by the dotted lines). The dotted lines in 1 and 2 are the spectral sensitivity of the photomultiplier.<sup>7</sup>



FIG. 2. Topogram (b) and current image (a) of a transverse cleavage face of a multilayer structure based on GaAs. Dimensions of the frame are  $630 \times 520$  nm<sup>2</sup>, range of variation of the z coordinate is 66 nm; change in the current was 1.8 nA upon switching the specimen-stylus voltage from -5 to +5 V.<sup>9</sup>

resonance excitation and light emission by impurity molecules was demonstrated in the same way. To do this, copper phthalocyanine was sputtered onto the surface of an Au film with a calculated thickness of  $\sim 1$  monolayer. In this case an extra emission at  $\sim 3.5$  V appeared, with this peak corresponding to generation of photons of energy  $\sim 2 \text{ eV}$  (Fig. 1). Apparently the mechanism of emission is: excitation of the known transition in the spectrum of phthalocyanine at 3.6 eV, and then a transition amplified by interaction with a surface plasmon of close-lying frequency to a level  $\sim 1.8$  eV, or from this level to the ground state.

Highly interesting possibilities that are opened up in photoluminescence in semiconductors were demonstrated in Ref. 8. There transverse cleavage faces of multilayer structures of GaAs-AlGaAs were studied. The cleavage faces were made in situ in a high vacuum. It was established that only the GaAs layers emitted at a voltage in the tunneling gap  $U_{\rm T} = -2$  V. The emission intensity rapidly declines when one shifts the stylus into the AlGaAs region-by about an order of magnitude in the first 100 nm from the boundary of the layers, and beyond this there is a more slowly declining "tail". Apparently this phenomenon involves the diffusion of energetic electrons into the GaAs layer, and thus it can serve for studying the relaxation of energy of electrons in semiconductors. One can localize GaAs layers by the method of STM luminescence with an accuracy of  $\sim 2$  nm and reveal layers 5-nm and even 2-nm thick.

3. Image contrast caused by a difference in volt-ampere characteristics. In multilayer structures layers can also be revealed with a resolution close to that of the photoluminescence method by the method of "current images", which is based on the difference in volt-ampere characteristics of the different layers.<sup>9</sup> In this case, even if the cleavage is made under atmospheric conditions, one can distinguish the layers of differing composition with a resolution of 5–50 nm (depending on the physical properties of the materials on the two sides of the boundary) and distinguish layers  $\sim 10$  nm thick (Fig. 2).

An important application of STM is the study of hightemperature superconductors (HTSCs). Although in an HTSC of the type Y-Ba-Cu-O the surface layer usually does not correspond in composition to the bulk, which makes it impossible to scan over the surface with atomic resolution, it has proved possible to obtain the distribution of the energy gap with a resolution of the order of 0.1  $\mu$ m, reveal its relation to the composition of the material, and establish the presence of inhomogeneities of the material at dimensions of the order of 0.1 to 1  $\mu$ m. For a HTSC of the type Br-Sr-Ca-Cu-O it was possible at low temperatures to observe a superstructure with a period of the order of 27 Å, i.e., to approach close to atomic resolution.<sup>10</sup>

- <sup>1</sup>V. S. Édel'man, Prib. Tekh. Eksp., No. 5, 25 (1989). [Instrum. Exp. Tech. (USSR) **32**, 993 (1989)].
- <sup>2</sup>O. Albreksten, D. J. Arent, H. P. Meier, and H. W. M. Salemink, Appl. Phys. Lett. 57, 31 (1990).
- <sup>3</sup>G. Cox, D. Szynka, U. Poppe, K. H. Graf, and K. Urban, Phys. Rev. Lett. 64, 2402 (1990).
- <sup>4</sup> Ph. Avouris, J. Phys. Chem. 94, 2246 (1990).
- <sup>5</sup> R. J. Hamers and K. Market, Phys. Rev. Lett. 64, 1051 (1990).
- <sup>6</sup>J. K. Gimzewski, B. Reihl, J. H. Combs, and R. R. Schlittler, Z. Phys. B 72, 497 (1988).
- <sup>7</sup> I. I. Smol'yaninov, M. S. Khaĭkin, and V. S. Édel'man. Pis'ma Zh. Eksp. Teor. Fiz. **52**, 830 (1990) [*JETP* Lett. **52**, 201 (1990)].
- <sup>8</sup>D. L. Abraham, A. Veider, Ch. Schonenberger, H. P. Meier, D. J. Arent, and S. F. Alvarado, Appl. Phys. Lett. **56**, 1564 (1990).
- <sup>9</sup>A. M. Troyanovskiĭ, M. S. Khaĭkin, and V. S. Édel'man, Pis'ma Zh. Tekh. Fiz. **13**, 1359 (1987) [Sov. Tekh. Phys. Lett. **13**, 568 (1987)].
- <sup>10</sup> A. P. Volodin, M. S. Khaikin, and G. A. Stepanyan, in High T<sub>c</sub> from Russia, World Scientific, Singapore a.o., 1989, p. 201.

Translated by M. V. King