Study of the surface of a LiF:F_2^- crystal at a subwave spatial resolution

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Photoelectron images of the end of the tip of a field-emission microscope at a magnification $\sim 3\times 10^4$ have been obtained by illuminating the tip, made of a LiF:F_2^- crystal, with the beam from an argon laser. The images found during illumination at different laser wavelengths are quite different. It can thus be asserted that a new method for studying surfaces has been realized: chemically selective projection photoelectron microscopy. The images found are analyzed in connection with results on the selective external laser photoelectric effect in LiF:F_2^- and other insulating crystals. © *1995 American Institute of Physics.*

Many problems in surface physics, microelectronics, biophysics, and elsewhere require research methods which make it possible to study the surfaces of various samples at a high spatial resolution and to identify molecules or other small structures on surfaces (i.e., methods which have a high "chemical selectivity"). The methods of field-emission microscopy (or field-ion-emission microscopy) and scanning tunneling microscopy offer a high resolution, down to the atomic scale, but their chemical selectivity is rather low.[1,2] In an effort to overcome this shortcoming, it has been suggested that selective laser photoionization of molecules adsorbed on the tips of field-emission microscopes be used.[3] Experiments which have been carried out, however, have revealed significant difficulties, which stem from desorption, decomposition, and migration of adsorbed molecules over the surface of the tip in intense laser fields (see Ref. 4 for a brief review of the experiments which have been carried out). A selective external laser photoelectric effect has recently been observed[4–8] for some insulating crystals (CaF_2:Sm^{2+}, LiF:F_2^-, ZrO_2:Nd^{3+} , among others). This effect has made it possible to formulate a new approach to the problem, along which one can overcome the difficulties inherent in a study of adsorbed molecules.[9] In this letter we are reporting the first observation of a chemically selective image of the surface of LiF crystals with F_2^- color centers at a spatial resolution higher than an optical wavelength.

The experimental layout is shown in Fig. 1. The microscope tips are made from LiF:F_2^- crystals synthesized at the Institute of General Physics, Russian Academy of Sciences, by a method of mechanical cleavage and etching in concentrated hydrochloric acid. Tips 3–5 mm long were attached with Wood's alloy to a metal electrode, to which a voltage $U = -2.5$ kV was applied. The beam from an argon laser with a power $W \simeq 15$ mW was focused on the end of the tip by a lens with a focal length $f = 17$ cm. Photoelectrons emitted from the surface of the tip were directed by an electric field to the

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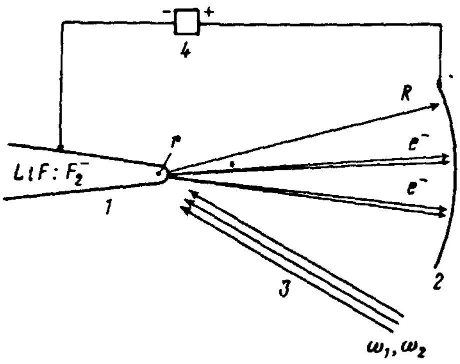

FIG. 1. Schematic diagram of a laser projection photoelectron microscope. 1—Microscope tip, made of the material under study; 2—microchannel-plate/fluorescent-screen assembly; 3—laser beam; 4—high-voltage source.

grounded input of a microchannel-plate/fluorescent-screen assembly at a distance $R \simeq 10$ cm from the tip. A vacuum $\sim 4 \times 10^{-7}$ torr was maintained in the test chamber. The optical image formed at the exit from the assembly was picked up by a TV camera connected to a Hamamatsu Photonics Argus-50 computer image-processing system. The experiment was controlled in real time by the computer.

The LiF:F_2^- test samples (with an F_2^--center concentration of 1.4×10^{16} cm^{-3}) had a significant conductivity, on the order of 10^{11} $\Omega \cdot$cm, so there was the hope of achieving a magnification

$$M \simeq \frac{R}{\chi r} \tag{1}$$

in the operation of this photoelectron microscope. This magnification would be analogous to that of a field-emission projector with metal tips.[1] Here r is the effective radius of curvature of the end of the tip, and the numerical value of the coefficient χ is in the interval 1.5–2. The curvature r and the magnification M were found by comparing a photoelectron image of tips and their images in atomic-force and electron microscopes. Expression (1) was confirmed qualitatively. Figure 2 shows photoelectron images of one of the LiF:F_2^- tips obtained during illumination of the tip by visible lines (Fig. 2a) and UV lines (Fig. 2b) from the argon laser. These images are very reproducible, and their intensities are many times the noise level. It can be seen from Fig. 2 that these images are quite different from each other and carry different types of information about the surface under study. On each image we can see some distinct bright photoemitting centers separated by a characteristic distance on the order of 100 nm. These centers are different in the cases of UV and visible illumination.

We believe that these results can be taken as demonstration of the first successful realization of a laser photoelectron projection microscope which combines chemical selectivity with high spatial resolution. Further research will be required to determine the nature of the photoemitting centers, but even at this point we can state that we have observed a selective external photoelectric effect for LiF:F_2^- crystals. The photoemission observed during the illumination of these crystals by laser light was caused by the direct

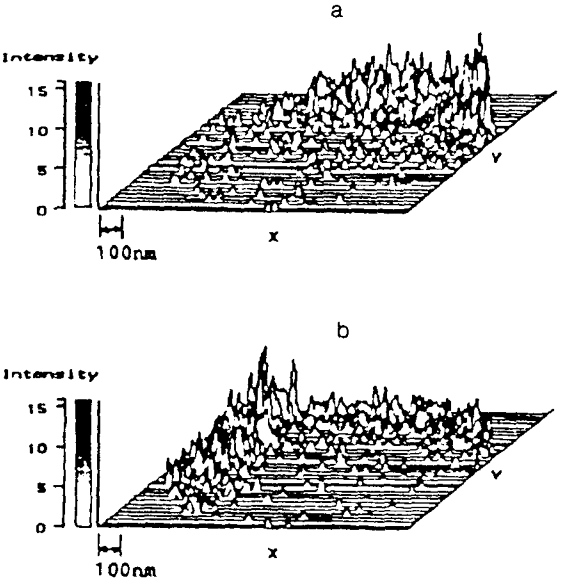

FIG. 2. Photoelectron image of the surface of a LiF:F_2^- tip with a radius of curvature $r \sim 3$ μm at a magnification $\sim 3 \times 10^4$. a—The tip was illuminated with visible light from an Ar^+ laser; b—with UV light from the Ar^+ laser.

one- or two-step photoionization of F_2^- color centers, while the photoemission observed from the surface of nominally pure LiF crystals under the same conditions was far less intense.[7,8] This result means that the photoelectrons observed under the corresponding experimental conditions are produced directly near the F_2^- color centers and that the detection of these electrons at a high spatial resolution makes it possible to visualize the positions of these centers on the surface of the LiF crystal. The average distance between F_2^- color centers in these samples was about 40 nm; for an electron emission depth on the order of 1–10 nm (Ref. 10), this distance corresponds to an average distance $l \sim 100$ nm between the photoelectron images of these centers. Since the photoemitted electrons have some transverse-motion kinetic energy E_0, the minimum resolvable distance is given by[3]

$$l_{\min} \simeq 2\chi r \left(\frac{E_0}{eU} \right)^{1/2}. \tag{2}$$

For $E_0 = 0.1$ eV and $U = 2.5$ kV, this minimum distance is ~ 60 nm. Since we have $l > l_{\min}$, it looks completely possible to observe individual F_2^- color centers under these experimental conditions.

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