Irradiation-induced nanometer-scale surface etching of a CdSe film with a scanning tunneling microscope

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Received 19 July 1990

Nanometer size features have been etched in a circa 200 Å thick CdSe film held in a scanning tunneling microscope (STM) by irradiation with a He–Ne laser (8 mW) with the STM tip biased to a positive potential. Etching does not occur in the absence of irradiation or with the STM tip biased negative. A tentative mechanism based on electrical field assisted photodecomposition is proposed.

1. Introduction

We report here the etching of the surface of a CdSe thin film on the nanometer scale using a scanning tunneling microscope (STM). This etch was carried out by pulsed laser irradiation of the semiconductor surface while a biased STM tip was held over a target area or scanned in a small pattern.

Since the invention of the STM [1], a number of reports of its use to produce nanometer-size surface modifications have appeared. Such nanometer-scale fabrication has potential applications in areas such as high-density information storage, high-resolution lithography, and the production of circuits and solid-state devices whose electric properties are governed by quantum-size effects. In this rapidly growing area, direct writing with the STM has already been realized [2–5]. Moreover, modification of a surface on the atomic scale [6] and manipulation of individual molecules, and even atoms, on a substrate have been reported [7,8]. Although the detailed mechanism of the modification or manipulation is not clear in many cases, the possibilities for perhaps the ultimate in device miniaturization are more evident then ever before. A variety of materials have been studied, for example, Au [4,9–14], Ag [15,16], Cu [17], Si [5,18–20], a-SiH [21], Ge [6], GaAs [22], M/Si (M = Au, Pt, Al, Cr, CaF_2, and AlF_3) [23,24] HOPG [25–27], $Pd_{81}Si_{91}$ [28], $Rh_{25}Zr_{75}$ [29], $Rb_{0.3}MoO_3$ [30], $Hg_{1-x}Cd_xTe$ [12], and $HoBa_2Cu_3O_{7-x}$ [31]. These modifications have been obtained using different methods, including (1) direct touching or scratching of the surface with the STM tip [9,12, 13,15,16,28]; (2) applying a high voltage or current across the tunneling gap [4,10,11,14,19,21,25,26, 29,31]; (3) electrochemical or chemical vapor deposition and etching with the STM [2,3,17,22]. Here we report a different approach for the surface modification of CdSe semiconductor films.

2. Experimental

The STM was a Nanoscope II (Digital Instruments, Inc., Santa Barbara, CA). The Pt/Ir STM tip was made by electrochemical etching following procedures described elsewhere [32]. The instrument was placed on a heavy plate suspended from the ceiling with rubber cords. The cover of the STM was modified to incorporate a small window (circa 2 cm × 2 cm) through which a 8 mW helium–neon laser with a beam diameter of 2 mm (Spectraphysics Inc., Mountainview, CA) could irradiate the sample surface. The STM was operated in air at room temperature. CdSe semiconductor films (circa 200 Å thick) were prepared by evaporating highly purified CdSe powder (99.999%, Aldrich Chemical Co., Milwaukee, WI) onto indium–tin oxide coated glass slides in a vacuum chamber (circa 5×10^{-7} Torr). There was no intentional doping or annealing of these films. Energy dispersive X-ray spectroscopy (EDS) of these films showed Cd and Se in about equal atomic concentrations. The energy gap was about 1.7 eV, as determined from the absorption spectrum of these CdSe semiconductor samples. The procedure for nanometer-scale etching was a follows. After a reasonably clear image of the semiconductor surface was obtained, the STM tip, without any interruption of the tunneling current, was moved to the desired location (for example, a high spot on the surface) and either held there or scanned in a small pattern. A pulse of laser irradiation (≈ 10 s) was directed at the sample surface under the tip. The surface was again scanned to image the original area, and the before-and-after laser pulse images compared to assess the extent of surface etching.

3. Results and discussion

A typical etch experiment is illustrated in fig. 1. Parts (a) and (c), grayscale and topographic images, respectively, of the CdSe surface before etching show a prominent peak at (x, y) coordinates (40, 30 nm) indicated by the arrow. The top of the peak was about 4 nm above its surroundings with base dimensions of about 7 by 12 nm. The tip, biased 2 V positive with respect to the CdSe, was positioned at

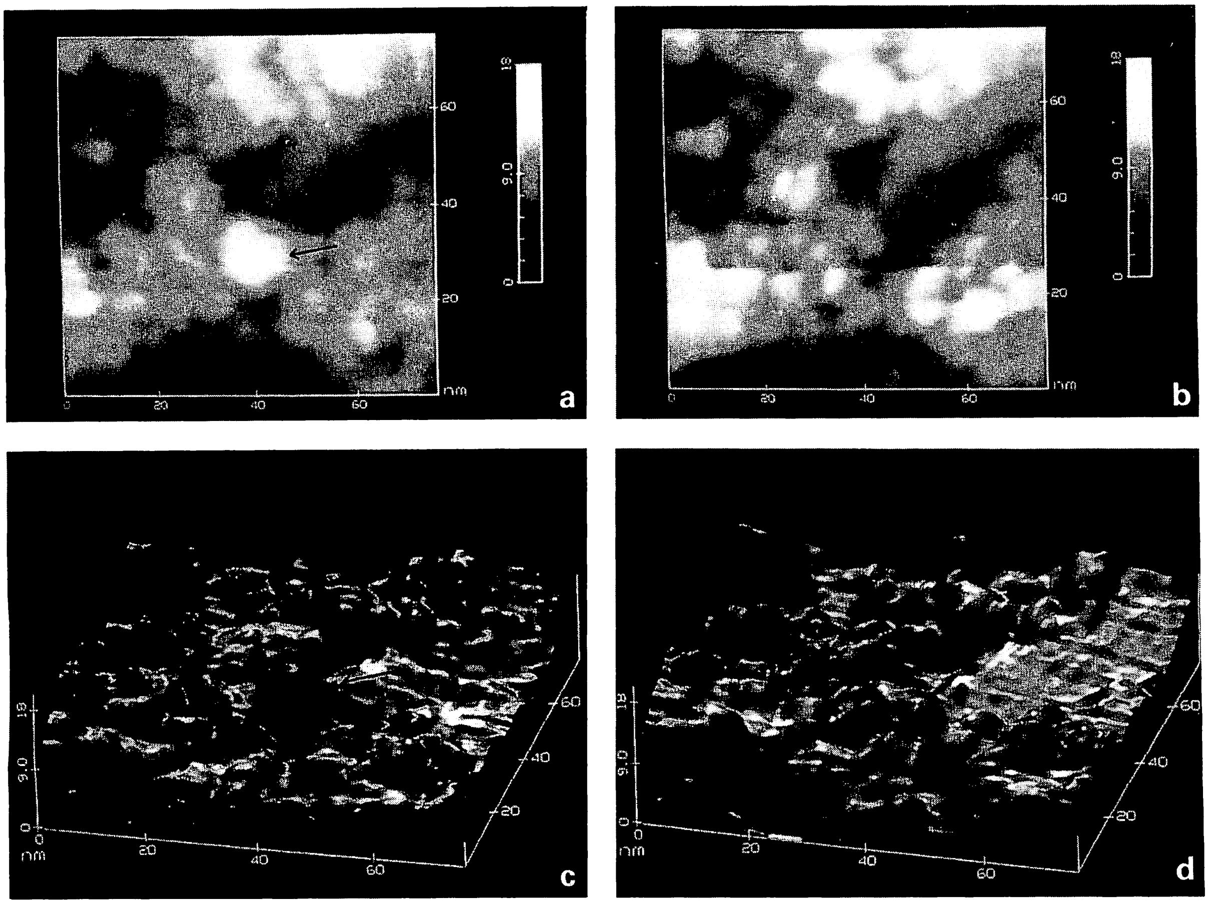

Fig. 1. Gray-scale (a, b) and topographic (c, d) STM images of a 200 Å CdSe film. (a) and (c) before etching; (b) and (d) after etching by application of a laser pulse with tip held over indicated peak. $I=0.21$ nA, $V=2$ V with tip positive.

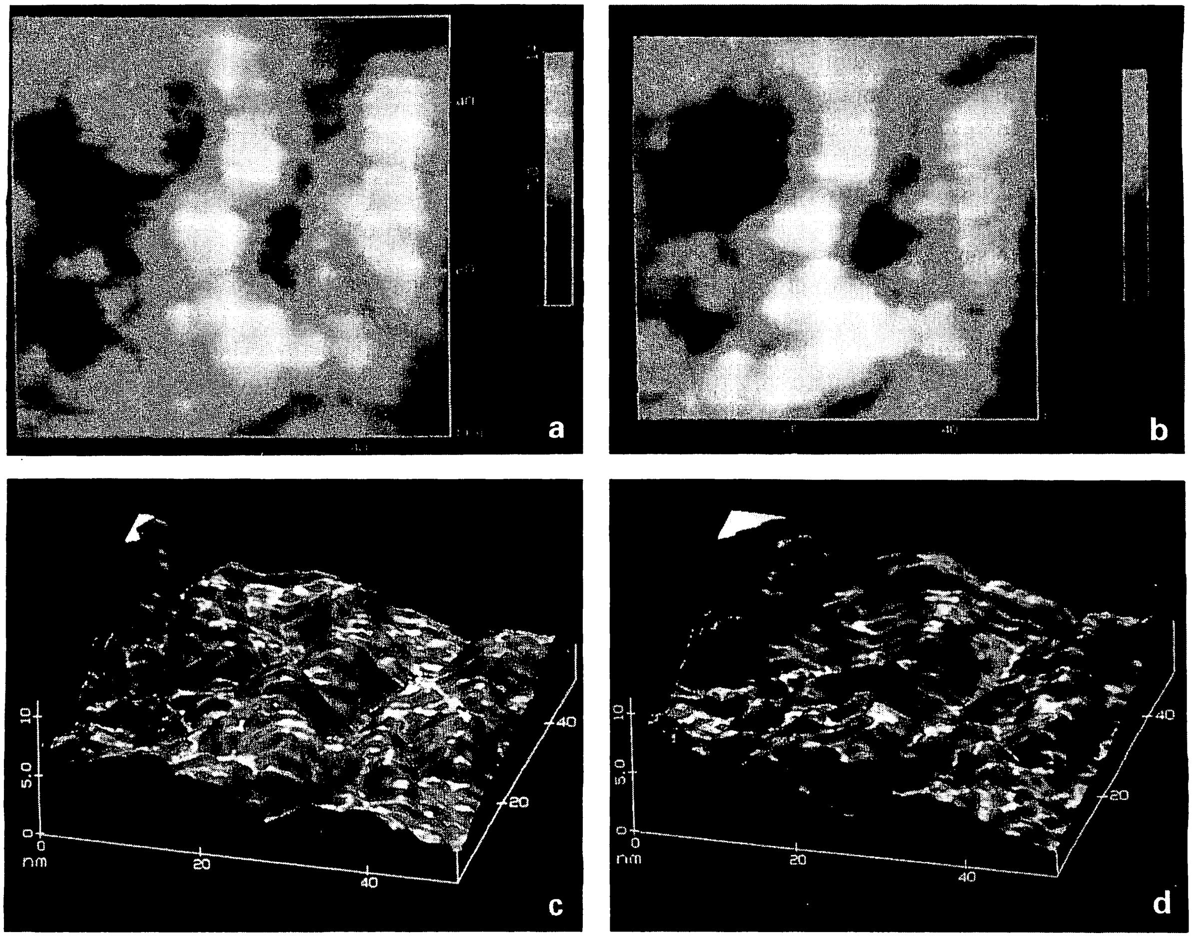

Fig. 2. Gray-scale (a, b) and topographic, (c, d) STM images of CdSe film. (a) and (c) before etching; (b) and (d) after etching with a laser pulse while a small square area was scanned in upper left quadrant of figures. $I=0.21$ nA, $V=2$ V with sample negative.

this peak and a laser pulse of 5 s directed at the tip. Figs. 1b and 1d show the result. The peak has disappeared and has been replaced by a small hole. There was essentially no drift of tip position after the laser pulse, since recognizable surface features in the areas away from the tip location during the laser pulse appeared at the same positions on the image. Holes could also be etched at other, smoother, locations on the surface by this procedure. No etch holes occurred in the absence of laser light, when the positively biased tip was held above a surface feature for several minutes. Similarly no etching resulted when the tip was biased negative, even with longer laser pulses. Fig. 2 shows similar etching results obtained by scanning a 10 by 10 nm area of the CdSe surface during circa 10 s of laser irradiation of the CdSe film. A roughly square etched crater appeared, shown in the upper-left corner of figs. 2b and 2d.

One possible mode of etching would be thermal expansion of the CdSe sample during the laser pulse so that the tip contacts the CdSe and pushes a hole into the surface. However there are several reasons why we feel this does not happen. The total thermal energy deposited by the 8 mW laser is small. For example, irradiation of a thermocouple causes less than a 2°C rise in temperature. Since the CdSe film is only 200 Å thick, such a temperature change would result in a thickness change of <0.02 Å, assuming a coefficient of thermal expansion of 3×10^{-5}°C^{-1}. Indeed a temperature rise greater than the melting point of CdSe (1512°C) would be required to cause the 10 Å expansion needed for a tip crash! Moreover, scans taken immediately following the laser pulse showed no evidence of tip damage and no etching was seen when the tip was negatively biased during irradiation.

The effect of the irradiation time and tunneling current on the etch pattern was not very clear, since the extent of etching depended strongly on the original geometric shape of the specific area under the tip on the substrate surface. Clearly the etched area was controlled by the tip–substrate field, and was much smaller than the irradiated area on the surface. The etching process did not disturb the portion of the CdSe around the tip and only small amounts of deposits could be observed in the vicinity of the etch spots. This seems to be a common observation in nanometer scale surface modifications with the STM. It is thus not clear where the CdSe removed from the surface goes. Some of the etched material might have been transferred to the tip through atomic forces or the strong electric field across the tunneling gap. For example, transmission electron microscope images showed that carbon fibers up to 1000 Å long and carbon clumps of circa 50 Å dimensions have grown at the end of an STM tip which had been scanned continuously over a graphite surface for one week [33]. Material transfer could also be seen from substrates, like Si, to an STM tip, with such transfer said to improve the resolution of the STM images [18]. We have no evidence however for any CdSe material forming on the tip after several etching experiments in our results. CdSe might be splashed away from the tip and deposited on remote areas of the substance.

We tentatively favor a "dry photoelectrochemical" process for the observed etching behavior. In this process the laser pulse causes photoejection of electrons from the semiconductor surface to the positively biased tip, leaving holes at the surface. This may cause local decomposition of the CdSe below the tip, before the surface holes are filled in with electrons from the CdSe contact, liberating positive CdSe ions (or decomposition of the CdSe). Note that the nearly intrinsic CdSe film is only about 200 Å thick, so that a space charge layer would not be expected in the film. Products are pulled away from the surface by the strong ($\approx10^7$ V/cm) electric field across the gap. In some ways this process resembles the well-known photoetching of semiconductors in liquid media [34], where ion formation is assisted by positive biasing of the semiconductor, which promotes hole migration to the surface and the occurrence of solvation and ionic charge compensation in the liquid phase. When the tip is biased negative in the dry photoetch process, the field direction would not favor electron emission from the semiconductor surface, since tunneling electrons are moving from the tip to the semiconductor. A given etch spot involves the removal of about 112 nm^3 of material or 2000 CdSe molecules. Since the photon flux is 8000 photons nm^{-2} s^{-1}, about 1700 photons impinge per CdSe removed, so the overall photoefficiency of the process is quite small ($\approx$0.1%).

In conclusion, we have described a new method of modifying the surface of a semiconductor with an STM and laser irradiation. Nanometer scale etch patterns on CdSe thin films have been demonstrated and a tentative mechanism of field assisted photodecomposition has been proposed.

Acknowledgement

The support of this research by grants from the Texas Advanced Research Program and NSF (CHE 8805685) is gratefully acknowledged.

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