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## The Surface of AgBr Thin Films Studied by Atomic Force Microscopy

Silver bromide is taken as a typical insulating sample in order to reveal the surface structure by atomic force microscopy (AFM). Terraced growth hills and screw dislocations on epitaxially grown AgBr(001) films have been observed. Typical step heights are found to be 2.9 Å which correspond to monatomic layers. At higher lateral magnification, atomic resolution shows a regular square lattice with a periodicity of 4.1 Å. As an instrumental contribution, the use of the force versus distance calibration curve is discussed.

### Introduction

The surface properties of silver halide crystals are of great interest, especially with respect to the photographic elementary process. The formation of the latent image is believed to start at charged kink sites and jogs on the surface. Electron optical methods have not yet been successfully performed on AgBr surfaces. They can cause charging effects, beam damages and photolysis, respectively. Using the method of surface decoration [1] detailed information of the silver halide surfaces has been obtained [2, 3].

With the atomic force microscope (AFM) it is possible to image AgBr surfaces down to atomic resolution [4, 5].

### Experimental

Epitaxial AgBr(001) films were grown by vapour deposition on cleavage faces of NaCl single crystals at a substrate temperature of 100 °C. The deposition process has been described elsewhere [4]. The presented measurements were performed with a NanoScope II AFM (Digital Instruments Inc.). Cantilever-type Si<sub>3</sub>N<sub>4</sub> springs with integrated tips and spring constants of 0.1 N/m were chosen as force sensors. Typical tip radii of curvature were 30 nm.

The AgBr surface turned out to be quite a delicate sample also for AFM. Surface modifications have been observed [6] as long as the measuring force has not been minimized. Due to this effect, the following section is devoted to a qualitative discussion of the force versus distance calibration curve (see also [7]).

A representative force versus distance curve on AgBr is shown in figure 1a. The deflections of the cantilever-spring are displayed in the vertical dimension and the horizontal axis represents the distance of the sample with respect to the default position of the cantilever-spring (without external force). This default position, in the following named "free cantilever", is marked by the white arrow (at the lower left) in figure 1a.

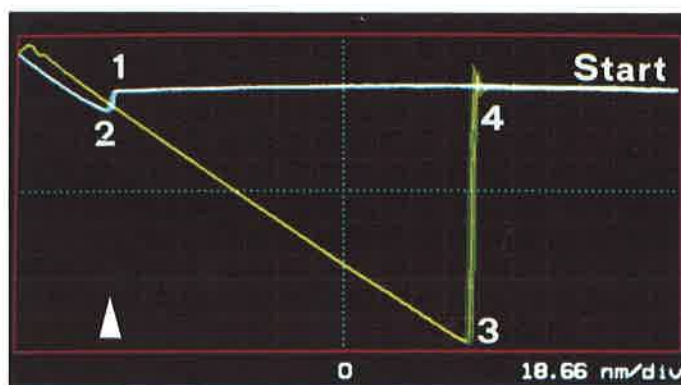


FIGURE 1a. - Force versus distance curve on AgBr(001). The white arrow marks the position where the sample reaches the free cantilever.

At the beginning of each calibration loop, the sample is far away from the free cantilever (at the right). The sample is approaching (white) and reaches the cantilever which jumps into the contact mode (from point 1 to 2). The tip remains in contact with the surface, even if the sample is pulled back far behind the free cantilever (green). At point 3 the loading of the spring becomes larger than the attractive interaction, so that the cantilever jumps off the surface into its free position 4.

Figure 1b shows a qualitative Lennard-Jones potential between a simplified tip (one atom) and an atom of the surface. Out of this graph the shape of the calibration loop can be roughly understood: during the approach, the setup becomes unstable at point 1 because the force gradient gets steeper than the spring constant  $c$  of the cantilever. The tip jumps to a different part of the potential curve 2. During the retraction, a similar instability is reached at point 3.

A more realistic measuring situation with an extended tip is drawn in figure 2.

Figure 2a shows the tip, sitting at the end of the cantilever-spring, just after a normal approach into contact mode. The cantilever is bent by a small repulsive total force. But what force is acting within the tiny imaging contact area between tip and sample? Due to the extent of the tip, a whole spectrum of gap distances exists. Quite a large part of the tip is in the attractive regime of the potential curve (see figure 1b). The sum of all attractive contributions  $A$  plus the force of the spring must be balanced by a strong repulsive force  $R$  in the contact area.

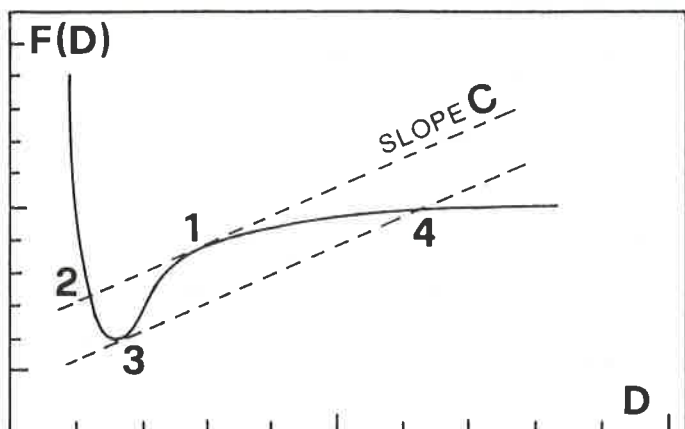


FIGURE 1b. - Lennard-Jones potential  $F(D)$  between idealized tip and sample. The spring constant  $C$  of the cantilever is represented by straight lines with slope  $C$ .

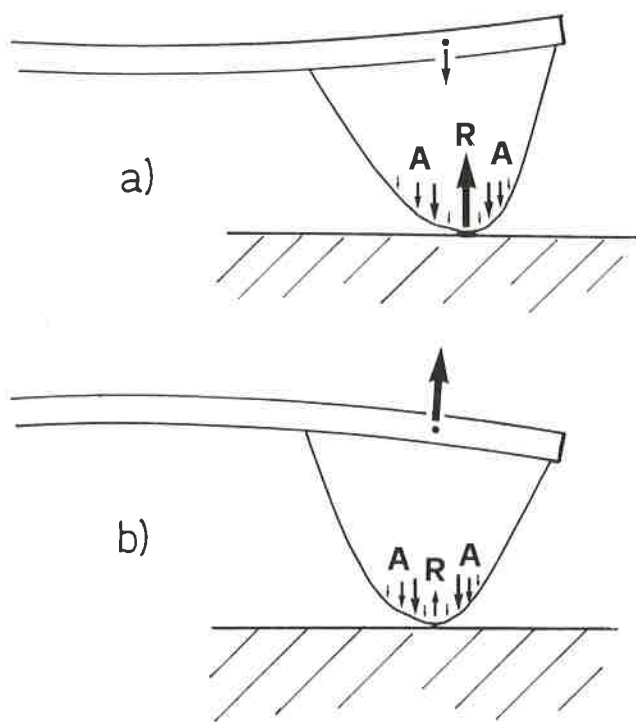


FIGURE 2. - Measuring situation with an extended tip : (a) just after approach and (b) after minimization of the force. Regions with attractive and repulsive contributions are labelled A and R, respectively.

Figure 2b shows the situation after minimization of the imaging force. The sample, with cantilever in contact, is pulled back close to the jump-off point (point 3 in figure 1a). Now, the attractive contributions A are balanced mainly by the deflected cantilever.

(In practice this retraction of the sample is achieved by lowering the setpoint voltage of the feedback electronics).

On fragile surfaces or soft samples this procedure of force minimization can be essential for obtaining a good contrast and for avoiding damages. Sometimes the attraction between tip and sample (in air) is so strong that a jump of the cantilever can not be observed within the travel of the piezo transducer. This can be caused by a weak spring constant of the cantilever or by some adsorption layers between tip and sample, resulting in strong capillary forces.

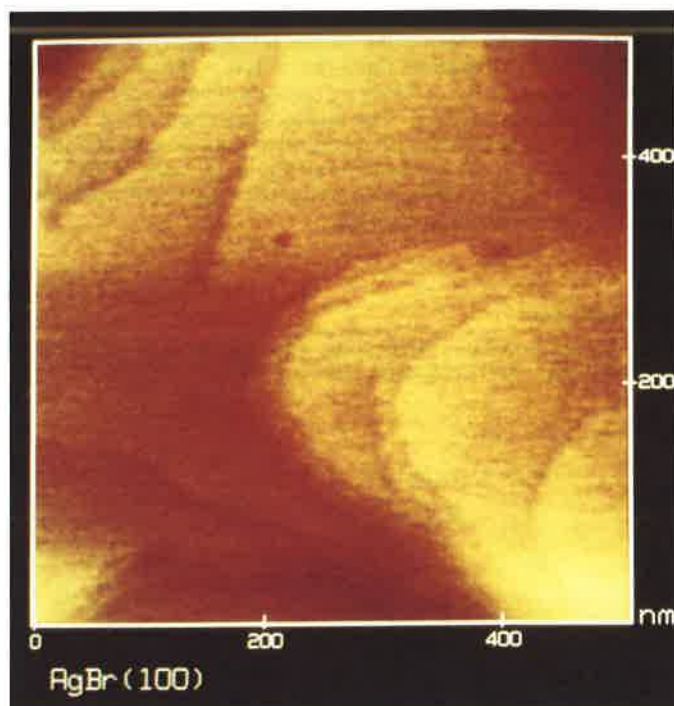


FIGURE 3. - Raw data of an AFM image on AgBr(001). Typical step heights are  $2.9 \text{ \AA}$ .

## Results

An AFM image of a  $0.5 \mu\text{m} \times 0.5 \mu\text{m}$  area of the AgBr(001) surface is shown in figure 3. Terraced growth hills and the emergence point of a screw dislocation (slightly right of the center) appear. The typical step height is  $2.9 \text{ \AA}$  which corresponds to monatomic layers. The morphology, mapped by AFM on a micrometer scale, agrees very well with the images obtained by the metal decoration [4].

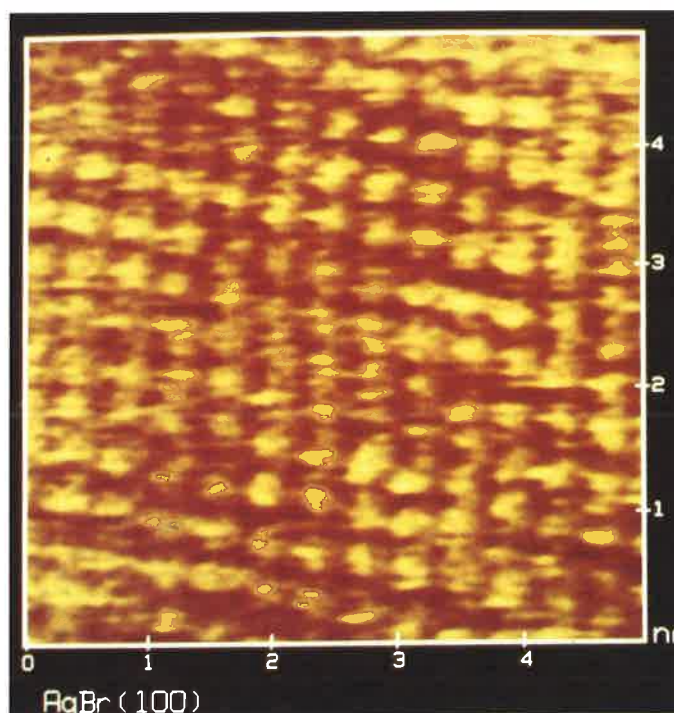


FIGURE 4. - Atomic lattice on the AgBr(001) surface. The dots are separated by  $4.1 \text{ \AA}$ .

Figure 4 shows a zoom into an area of  $5 \text{ nm} \times 5 \text{ nm}$  on a flat terrace. It reveals the square-like atomic lattice with a spacing of  $4.1 \pm 0.2 \text{ \AA}$ . The corrugation along the  $\langle 100 \rangle$  directions is determined to be  $1.0 \pm 0.5 \text{ \AA}$ . Atomic resolution has not been achieved in the vicinity of steps. The lattice separation of  $4.1 \text{ \AA}$  corresponds well to the spacing between two equally charged ions in the bulk of AgBr. A comparison of the ionic radii of  $\text{Ag}^+$  ( $1.15 \text{ \AA}$ ) and  $\text{Br}^-$  ( $1.96 \text{ \AA}$ ) [8] suggests that the AFM contrast is dominated by the larger bromine ions.

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## References

- [1] G.A. Basset, *Phil. Mag.*, **1958**, *3*, 1042.
- [2] H. Haefke, M. Krohn, A. Panov, *J. Cryst. Growth*, **1980**, *49*, 7.
- [3] H. Haefke, R. Mattheis, M. Krohn, *Thin Solid Films*, **1980**, *195*, 225.
- [4] H. Haefke, G. Gerth, M. Krohn, E. Meyer, H.J. Güntherodt, *J. Imaging Sci.*, **1991**, *35*.
- [5] E. Meyer, H.J. Güntherodt, *Europhys. Lett.*, **1991**, *15*, 319.
- [6] E. Meyer *et al.*, submitted for publication.
- [7] H. Hug, Th. Jung, H.J. Güntherodt, submitted to *Rev. Sci. Instr.*
- [8] P.W. Atkins, *Physical Chemistry*, p. 750 (Oxford University Press, **1982**).