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In situ AFM, XRD and resistivity studies of the agglomeration of sputtered silver nanolayers

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Abstract

In situ atomic force microscopy (AFM), X-ray diffraction (XRD) and resistivity studies have been made for RF cathode-sputtered silver nanolayers on different oxide surfaces during heating between room temperature and 400°C. Our earlier AFM and resistivity measurements revealed the agglomeration of layers during heating. The present *in situ* AFM, XRD and resistivity measurements show a sudden rapid agglomeration of the sputtered ultra-thin silver nanolayers during heating at specific temperatures, which depend on the layer thickness. When the AFM picturing was initiated from a layer surface at a temperature slightly below the specific agglomeration temperature of the layer, the AFM tip excited the surface starting the agglomeration in the area under picturing. This tip-assisted agglomeration phenomenon made it possible to restrict the area of agglomeration and to produce sub-micron structures in the silver nanolayer by AFM.

Introduction

Catalytically active noble metal surfaces are used in semiconductor gas sensors (and also in calorimetric gas sensors) as metal-cluster deposits to increase the selectivity and sensitivity, and to reduce the response and recovery times of the sensors (Lantto, 1992). Almost all selective sensors with short response times contain catalysts. Palladium, silver platinum and gold are the usual noble metal catalysts, which are used as surface additives on oxide semiconductors to improve the gas-sensing properties of gas sensors based on these oxides.

Semiconductor gas sensors operate at elevated temperatures (typically in the range of 150–450°C) where an oxidation of also some of the noble metals, such as palladium, is possible. Ultra-thin noble metal layers made, e.g., by sputtering are an important step in the fabrication of semiconductor gas sensors with thin-film technology, since they can be converted to catalytic nano-particles on the thin-film oxide surface by heat treatment (Mizsei, 1993). Silver-catalysed SnO_2 sensors have been found to have optimum properties for the monitoring of volatile sulphides, such as H_2S, which is a pollution agent in city air (Lantto & Mizsei, 1991); Harkoma-Mattila et al., 1992).

Supported catalysts can affect the conductance response of semiconductor gas sensors through two main mechanisms. The first mechanism is the spill-over of activated reactants from the catalyst onto the semiconductor support. In this case, the activated reactants can inject electrons into or extract electrons from the semiconductor. The second mechanism is the Fermi energy control, where the catalyst itself injects electrons into or extracts electrons from the semiconductor support.

A general discussion of the agglomeration phenomena of metal films (formation of separate particles from a continuous film) has been given by Maissel (1970),

and in the case of silver films by Sharma (1980). There are only a few reports of direct observations of the agglomeration phenomena of catalytic noble metal layers on supporting oxides, and no reports of *in situ* studies of these physical processes. Atomic force microscopy (AFM), however, is now a very effective tool for an *in situ* study of these phenomena. In this work we have used AFM to investigate *in situ* the agglomeration of sputtered silver nanolayers during heating and the morphology of the films before and after agglomeration. In addition, monitoring of layer resistivity and reflection peak intensities in the X-ray diffraction (XRD) pattern from the layer during heating were used as other *in situ* methods for the study of the agglomeration process of layers.

Experimental

Ultra-thin silver layers were RF-sputtered (without substrate heating and using a 13.56 MHz RF diode system, disc target, and power density of 0.5 W/cm^2 in pure argon). Thermally oxidised silicon slices (see later, as mini hot plate) and glasses (Corning 7059) were used as substrates.

The ultra-thin silver layers were structured after sputtering by scratching them with a sharp stainless steel (standard type hypodermic) needle in laboratory atmosphere. AFM images of structured surfaces are more informative, since the structuring makes it possible to compare between covered and uncovered substrate areas, and to measure, e.g., the layer thickness. Table 1 summarizes some information of the sputtered Ag layers on glass substrate.

All experiments have been performed in atmospheric environment, as the main purpose of our investigation is strongly connected with the activation of the

Table 1. Thickness (from AFM imaging), square resistance and agglomeration temperature of silver layers sputtered with different sputtering times (power density 0.5 W/cm^2) on glass substrate

Sputtering time (s) (40 W, 0.5 W/cm^2)	Thickness (nm) (AFM) as sputtered	Square resistance (Ω) as sputtered	Agglomeration temperature (°C)
20	6–7	2×10^5	~100
30	10	190	130
40		11	200
50	19	8	280
100	23	4–5	330
200	41	2–4	350

semiconductor gas-sensor surfaces. The surface morphology has been investigated by Digital Instruments Nanoscope II type equipment in AFM mode. STM was not suitable for our investigation, because the voltage on the heating resistor disturbed the tunnel current, and the resistance changed suddenly from several ohms to infinitely high. We are trying to solve these problems using SnO_2 covered substrate and better-structured hot plate, where the heating resistors are more separated from the silver layer.

The surface temperatures of the hot plates have been measured by a thermocouple attached to a digital thermometer. The estimated error in temperature is about 10°C.

Results and discussion

The surfaces of the as-sputtered ultra-thin silver layers were smooth with only a few clusters, as it is seen in the AFM picture in Figure 1(a). Our earlier measurements with a vibrating capacitor (Kelvin probe) displayed also that ultra-thin noble metal layers after sputtering form a continuous surface coverage, even at very low layer thickness (d), down to $d < 1$ nm (Mizsei, 1993). The cross-section AFM profile from the structured surface in Figure 1(b) indicates the layer thickness (~10 nm). The width of the (1 1 1) reflection peak in the XRD pattern in Figure 1(c) discovers the small grain size (23 nm from Scherrer's formula) in agreement with the AFM picture in Figure 1(a).

In situ resistance measurements of the silver layers on glass substrate with platinum contact pads were made during heating of layers on a hot plate and also in a temperature-controlled closed gas chamber. During heating, the layer conductance dropped suddenly down, practically to the value zero, as shown in Figure 2. The starting temperature for this sudden rapid agglomeration behaviour of an ultra-thin silver layer depends strongly on the layer thickness (compare the sputtering times of layers in Figure 2 with the thickness values in Table 1). After agglomeration, the layer surfaces were very rough, as it is seen in the AFM pictures in Figures 2 and 3, and also in the cross-section AFM profile in Figure 3(b). The XRD pattern in Figure 3(c) reveals also an increase of the grain size in the agglomeration process (50 nm from Scherrer's formula) in agreement with the results in the AFM picture in Figure 3(a) (compare with the corresponding results in Figure 1). A strong orientation of the grains in the ⟨1 1 1⟩ direction is also possible to see from

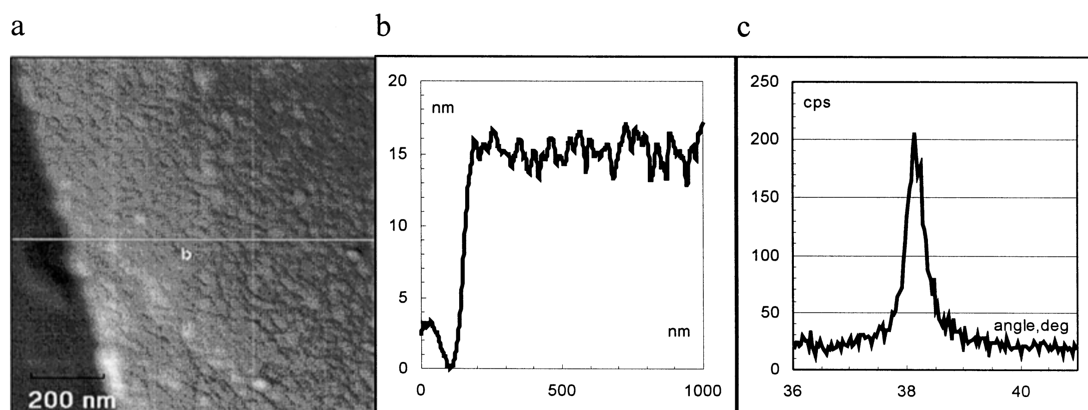

Figure 1. AFM picture (a), cross-section AFM profile shows the layer thickness (~10 nm) (b), and XRD pattern (CuK_α radiation) (c) from an ultra-thin silver layer after sputtering.

the XRD pattern in Figure 3(c). The layer in Figure 3 consists of agglomerated particles isolated from each other and, therefore, the conductivity of the layer is zero.

Our earlier XPS results (Mizsei, 1993) from similar surfaces of sputtered noble metal layers are in agreement with the above results. The surface coverage of as-sputtered ultra-thin silver layers ($d < 10$ nm) was interpreted from the XPS results to be 100%. After agglomeration, the interpreted fractional surface coverage dropped below 10% in the case of silver layers without showing any sign of oxidation.

Figure 4 shows an *in situ* XRD monitoring of the peak intensity of the (1 1 1) reflection during heating of a silver layer. The rapid increase in the peak intensity relates to the rapid agglomeration process of the layer. The value of 200 cps (count per second) before the agglomeration corresponds to the peak intensity in Figure 1(c), while 3500 cps at the end of heating is about the same peak intensity as in Figure 3(c).

The specific temperature is the most important (critical) parameter of the agglomeration. As the process is very quick, we cannot observe more exact time dependence. However, the heating rate has no strong effect on the agglomeration.

The above detailed observations suggest that the melting and re-crystallisation of the layer are the basic physical processes behind the silver agglomeration. Accepting that statement, the thickness dependence of the agglomeration temperature can be explained by the size effect on the melting point (Greer, 1992). The same effect has been found for Au (Greer, 1992) and Bi (Patterson et al., 1992) nano-particles.

For *in situ* AFM monitoring of the agglomeration phenomena, a miniature hot plate, shown in Figure 5, was constructed. An iron plate in the construction in Figure 5 fixes the sample holder magnetically to the AFM scanner. Two quartz plates isolate the heat from the scanner, while an oxidized silicon substrate slice gives a good electrical isolation and also a low heat resistance, resulting in a homogeneous distribution of the surface temperature. A thin platinum film is used as a heating resistor in the hot plate construction.

The excitation effect of the AFM tip on the agglomeration of a silver layer is shown in Figure 6. A hot layer surface about 20°C below the agglomeration temperature of the layer was scanned many times at the black area on the right, where the tip has started the agglomeration and almost completely removed the silver layer from the scanned area. In the middle of Figure 6. it is possible to see how the agglomeration has just started in a square area after a few AFM scans. In the case of small scanning areas, the excitation effect of the tip was still more intensive. In the upper corner on the left in Figure 6, traces of two small scanned areas are seen. The silver layer has completely agglomerated and mainly removed as large particles on the border of the scanned areas. However, some particles are also seen even in the middle of the areas. After a scan on a large area, a full agglomeration is not achieved and a minimum number of scans is necessary for a full agglomeration of the scanned area. Two large area traces are also seen in Figure 6 where the numbers of scans have been below the numbers that were needed for a full agglomeration of these layer areas.

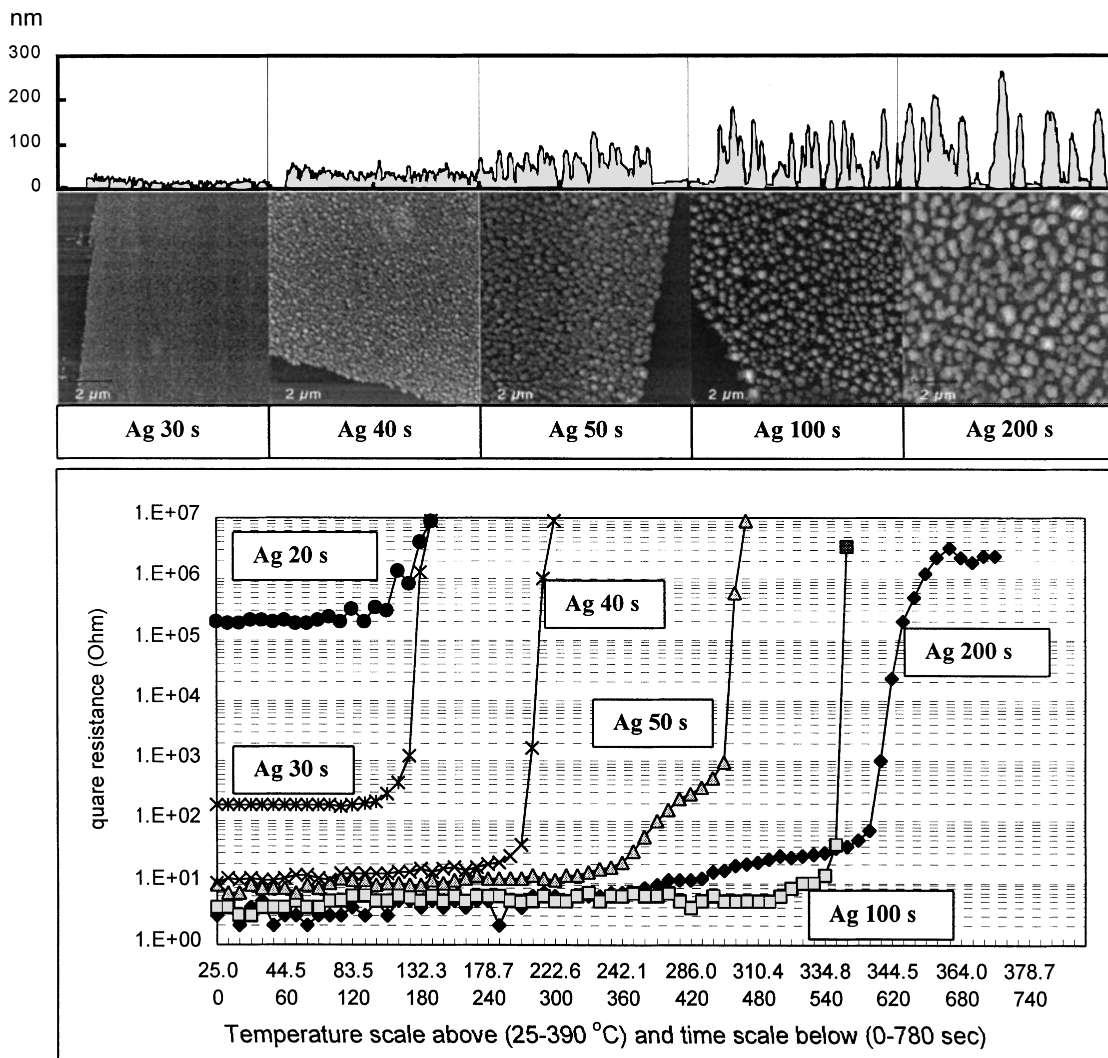

Figure 2. Square resistance of sputtered silver layers with different sputtering times (layer thicknesses in Table 1) as a function of heating temperature and time. The upper AFM pictures together with the cross-section AFM profiles are taken from the corresponding layers after heating. (Hot plate experiments, the heating rate is about 0.5°C/s, see the time and temperature scales).

Figure 7 reveals the mechanism of the tip-assisted material transport ('peeling off') during the AFM scanning of a silver layer. The AFM picture in Figure 7 shows a three-window sub-micron structure in the silver layer. The structure was fabricated by several AFM scans on a $2500 \times 2500\,\mathrm{nm}^2$ square area. During the repetitive scanning process, the material was pushed in a direction by the tip. When the amount of the accumulated material before the tip outgrows a critical mass, the tip is not capable anymore to move the material and a solid barrier starts to increase at the window border in Figure 7. Shaded areas of these barriers are also clearly seen in the AFM picture in Figure 7(a). The cross-section AFM profile in Figure 7(b) shows that all the material, which was removed from the window areas, is collected in the barriers at the window borders.

A more detailed description of the agglomeration process and tip-assisted material transport is shown in the sequential AFM pictures in Figure 8. In the first picture, in the left upper corner, the agglomeration has started and only one particle is picked up. This particle is moved to the left direction during the scan, and

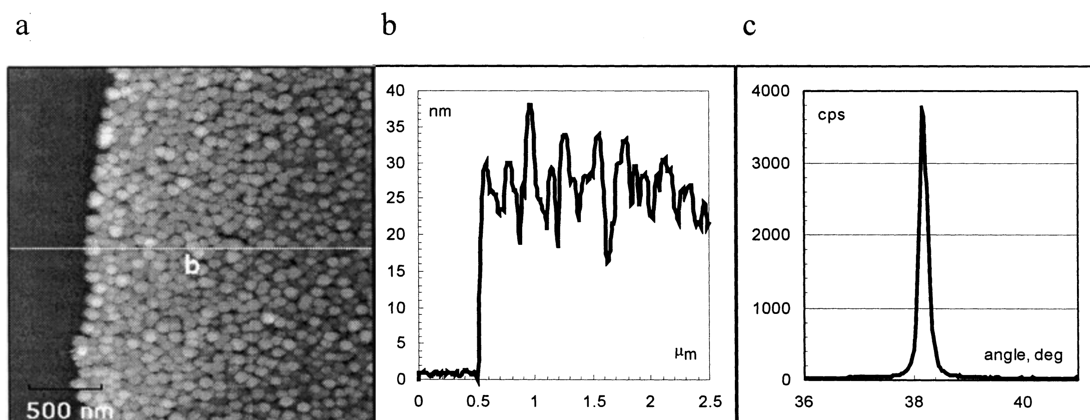

Figure 3. AFM picture (a), cross-section AFM profile (b), and XRD pattern (CuK_α radiation) (c) from an ultra-thin silver layer after the agglomeration process. The ∼10 nm (as sputtered) continuous layer is converted to over 20 nm discontinuous layer during agglomeration.

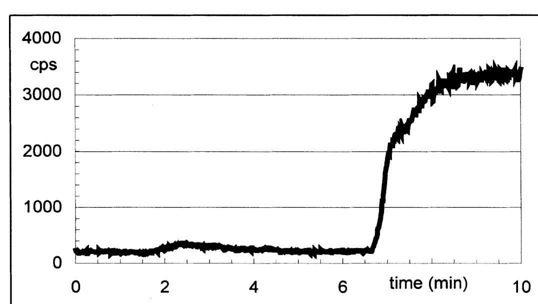

Figure 4. The peak intensity of the (1 1 1) reflection in the XRD pattern from an ultra-thin (30 s sputtered, ∼10 nm) silver layer as a function of heating time (the temperature has not been measured during this experiment, see Figure 2 for the corresponding heating temperatures).

pushed away from the scanned area during the repeated scanning. A larger moving particle is seen in the second picture on the right in three different positions. There are more mobile particles in the third, fourth, fifth, and sixth pictures, and the silver-free area is growing gradually. The size of the particles is also increasing with continued scanning. In the last six pictures, it is possible to see some further material rearrangement, and the final result is an almost silver-free scanned area. Figure 9 shows still another example of sub-micron structures that is possible to be fabricated by AFM scanning on a hot silver nanolayer at temperatures slightly below the agglomeration temperature of the layer.

Conclusions

In situ AFM, XRD and resistivity studies have been made of the agglomeration phenomena of sputtered silver nano-layers on oxide substrates. A sudden rapid agglomeration process was found to start, during heating of a silver nano-layer, at a specific agglomeration temperature that increased with the increasing layer thickness (Figure 10). *In situ* AFM studies of the layers during heating revealed a possibility to start the agglomeration by the AFM tip excitation at temperatures slightly below the agglomeration temperature of the layer. This observation made also possible to use AFM scanning to produce different sub-micron structures from the silver layers on the substrate. Not any oxidation of the silver layers was found by XRD during heating the layers up to 400°C.

The obtained results are very useful for the development of reproducible methods to fabricate proper silver-catalysed semiconductor gas sensors based on oxide semiconductors, such as tin dioxide. Especially the case of the Fermi energy control needs a high and uniform catalyst particle coverage, where the separate particles are near to each other, but do not shunt the high resistance of the semiconductor support. The understanding of the agglomeration process is of great value for the proper fabrication of catalysed thin-film sensors, since the dispersion together with the size and shape of the catalyst nano-particles have the central importance for the proper catalyst function (Valden et al., 1998).

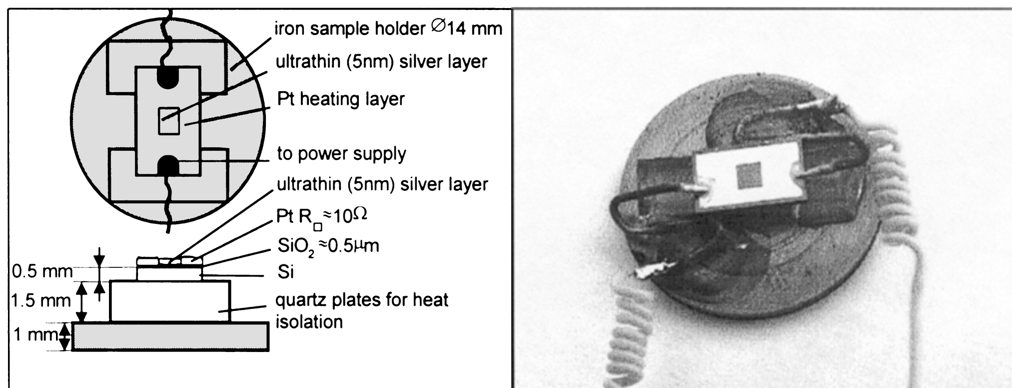

Figure 5. Drawing and photograph of the miniature hot plate used for *in situ* AFM studies. This model is not suitable for STM, because the area under investigation is not isolated from the Pt heating layer. Moreover, as the SiO_2-Si substrate is very good isolator, it is impossible to investigate the agglomerated layers by STM.

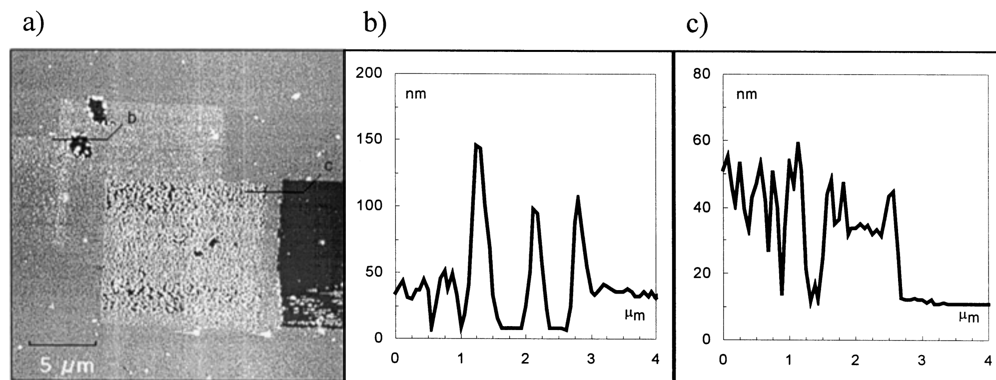

Figure 6. AFM picture (a) together with two cross-section AFM profiles, (b) and (c), from an ultra-thin silver layer ~l0 nm as sputtered on SiO_2-Si substrate) after different repetitive AFM scanning processes at a temperature (~110–120°C) slightly below the agglomeration temperature (130°C) of the layer.

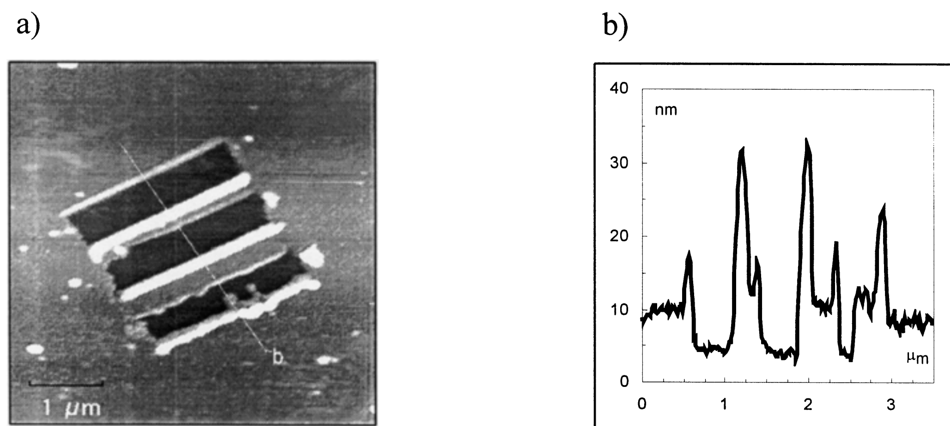

Figure 7. Peeling off the layer from the SiO_2-Si substrate by the AFM tip: AFM picture from a three-window submicron structure (a), together with cross-section AFM profile (b). The structure was fabricated from a 5 nm silver nano-layer by a repeated AFM scanning process on a 2500 × 2500 nm^2 area at a temperature (~100°C) slightly below the agglomeration temperature of the layer.

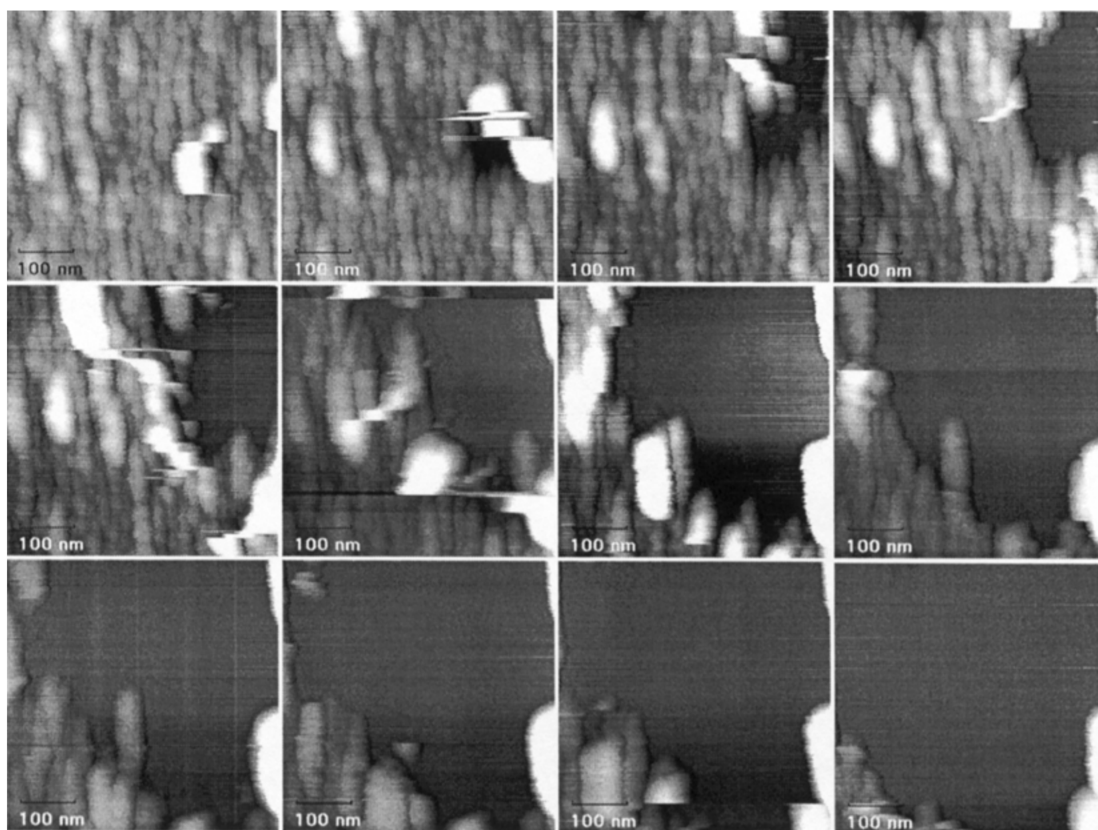

Figure 8. Sequential AFM pictures taken during a repeated AFM scanning process of a silver nanolayer (~10 nm as sputtered on SiO_2-Si substrate) at a temperature (~110–120°C) slightly below the agglomeration temperature of the layer.

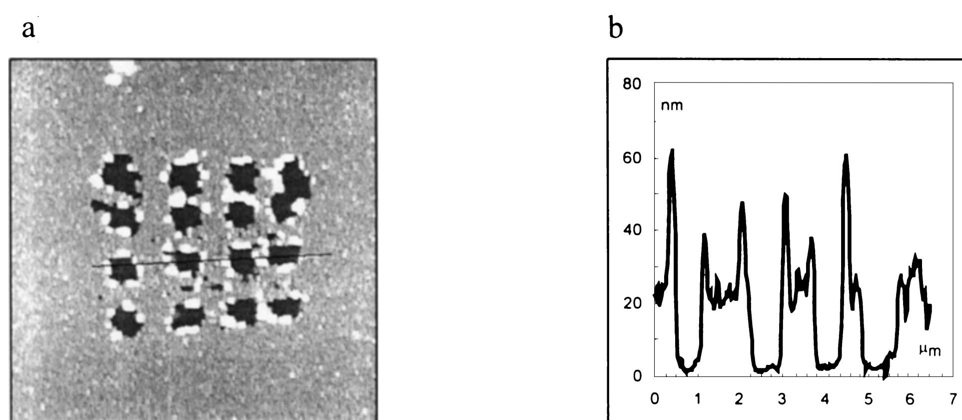

Figure 9. An example of submicron structure (AFM picture (a) and cross-section AFM profile (b)) fabricated by AFM tip-assisted agglomeration and material transport in a silver nanolayer (~l0 nm as sputtered on SiO_2-Si substrate).

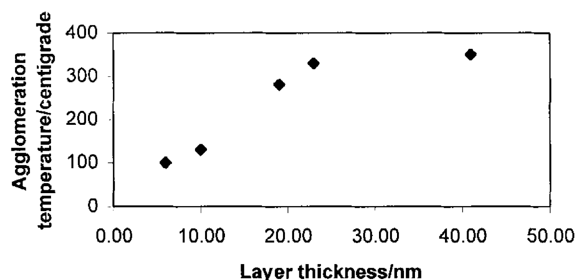

Figure 10. The dependence of the agglomeration temperature on the (as sputtered) layer thickness.

Acknowledgements

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