Nanotechnology 9 (1998) 352–355. Printed in the UK PII: S0957-4484(98)94923-6

Conductive SPM probes of base Ti or W refractory compounds

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Received 8 June 1998

Abstract. The results of investigations of W_2C, TiN, TiO_{2-x} thin films as prospective materials for conductive SPM probes in a silicon cantilever are presented. The ultrathin (1.5–10 nm) films are characterized by high conductivity, increased adhesion to silicon and chemical passivity. It is shown by means of conductive SPM measurements that there is no dielectric layer on the film surface and the conductive metal-coated silicon cantilevers were wear-proof.

1. Introduction

Scanning probe microscopy (SPM) with a conductive probe is used for investigating both surface morphology and electronic properties. This technique combines the best properties of scanning tunnelling microscopy (STM) and atomic force microscopy (AFM). In contact-mode AFM the conductive probe measures both the surface relief and the current between the tip and the surface which means that height images and spreading resistance images can be obtained simultaneously [1–6]. SPM with a conductive probe is called scanning resistance microscopy (SRM) [4] or scanning electrical conductivity microscopy (SECM) [3]. Henceforth we will call this technique SECM. SECM techniques used by different groups are, in general, very similar and can be distinguished only in the details [3, 6].

The efficiency of SECM research depends on which conductive probes are used. No universal probes exist to solve all the problems that develop in SECM. The most useful conductive probes are fabricated from hard materials (W, Mo, Ti) or from silicon or silicon nitride coated by an ultrathin metallic film [4]. However, the presence of a native oxide on the tip surface influences the results of electrical measurements. To provide a non-oxidized surface on a conductive material or high chemical stability, noble metals (Pt, Au) are used [1]. These metal-coated probes are characterized by low wear capability and low electromigration stability. In this case when the surface to be investigated is coated with a native oxide film (for example, a silicon substrate), the probe's bases are used. Such probes are able to work at pressure which is necessary to penetrate through the oxide. Sometimes probes are fabricated from ion-implanted diamonds or chemical vapour-deposited ion-doped diamonds [2, 3]. However, diamond probes have a high electrical resistivity. Moreover, diamond-based probes have a tip curvature radius of ~100 nm which limits the minimal size of the objects to be examined.

Thus, to increase the efficiency of SECM-based investigations it is necessary to search for more universal materials for use in conductive probes.

2. Experiment

In this work, the results of research into the use of W_2C, TiN, TiO_{2-x} (where $x < 0.5$) as coating materials for conductive probes based on silicon cantilevers are presented.

From the above analysis [1–6], the following requirements are necessary for the material for conductive coating of SECM probes:

- high hardness,
- high electrical conductivity,
- non-oxidized surface,
- high resistance to electromigration
- low thickness (2–10 nm),
- high adhesion to Si and Si_3N_4,
- chemical passivity.

It is known that carbides, nitrides and oxides of W and Ti have enhanced hardness and a high melting point [7]: $T_{\mathrm{melt}}(W_2C) = 3028\,^\circ C$, $T_{\mathrm{melt}}(TiN) = 3220\,^\circ C$, $T_{\mathrm{melt}}(TiO_{2-x}) = 2130\,^\circ C$. The resistance of materials to electromigration is directly proportional to the melting point, therefore these materials have high electromigration stability. Thus, conductive coatings based on these materials must potentially possess high wear capability.

Soft silicon cantilevers (force constant 0.5 H m^{-1}) were fabricated by means of microelectronic technology (lithographic processes, local anisotropy etching of silicon, thermal diffusion of boron, thermal oxidation of silicon) described elsewhere [8]. The surface concentration of B in silicon was $\sim 1 \times 10^{20}$ sm^{-3}. The cantilevers had a tip curvature radius of ~10 nm. The angle of the wall tips at the top was ~20°. The height of the cantilever tip was approximately 10 μm. Scanning electron microscopy (SEM) images of the silicon cantilevers are

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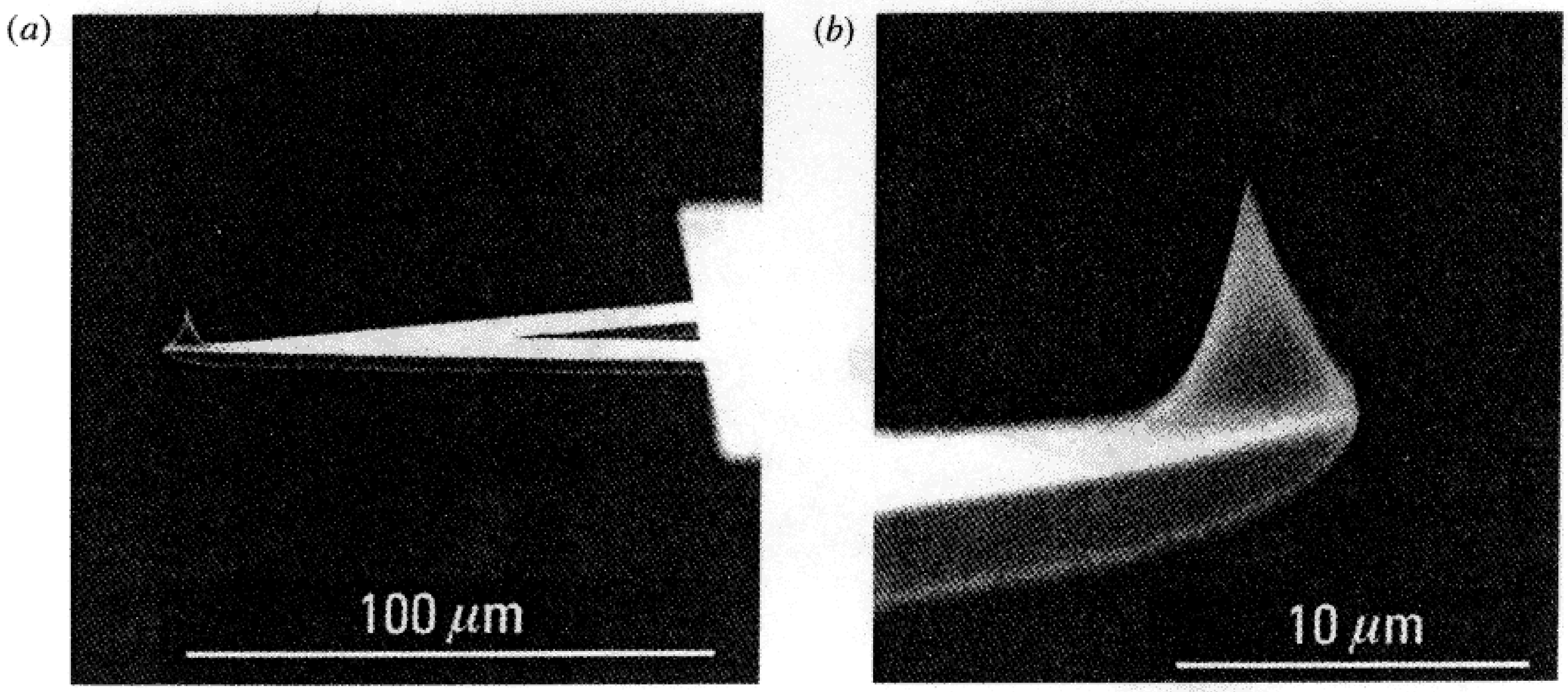

Figure 1. SEM image of the silicon cantilever: (*a*) general view of cantilever; (*b*) the image of tip.

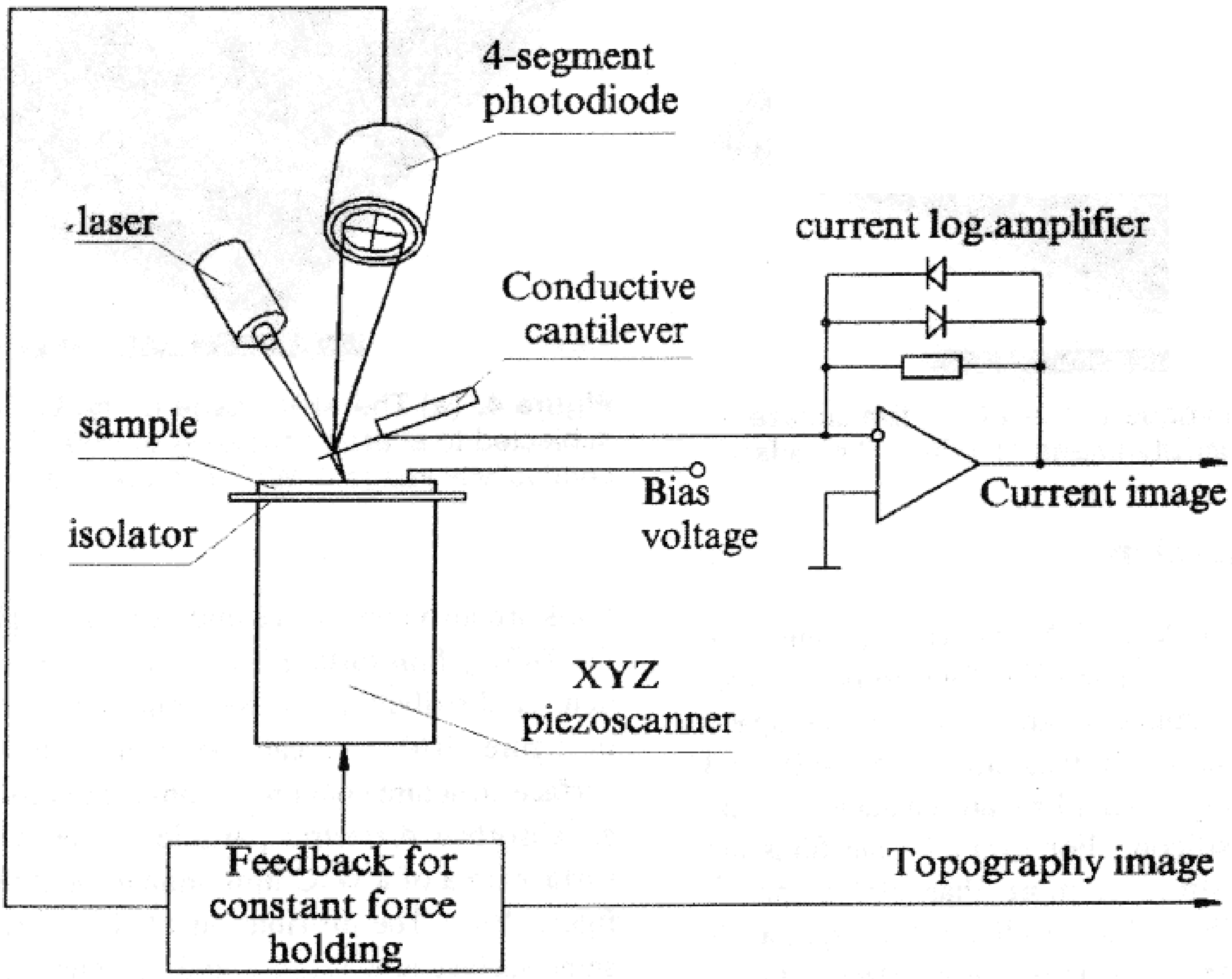

Figure 2. A schematic diagram of an electrical conductivity circuit.

presented in figure 1, where (*a*) is a general view of the cantilever and (*b*) is the image of the tip. For SEPM investigations, the silicon substrates and cantilevers were coated with a Ti or W film, 1–10 nm thick. The targets were fabricated from 99.999% Ti or 99.999% W. The metals were deposited using a cathodic arc deposition method [9]. W_2C, TiN, TiO_{2-x} (where $x < 0.5$) were then formed by annealing in the respective gases. The technological parameters and electro-physical properties of the films prepared in this way on silicon cantilevers were investigated.

The efficiency of the conductive cantilevers was studied by means of scanning probe microscope P4-SPM (NT-MDT, Russian Zelenograd). The conductive surface (graphite) to be tested was scanned with the AFM in contact mode using conductive cantilevers and the current between the tip and the surface was simultaneously measured (SEPM technique). The scheme for current measurements is shown in figure 2. The investigated surface was earthed whereas the surface of the conductive cantilever was positive. The measurements were carried out in air. The morphology and electrical conductivity of ultrathin (1.5–10 nm) conductive films deposited on silicon substrates were also investigated by SECM. Such investigations were also carried out on the films after thermal annealing at 900 °C.

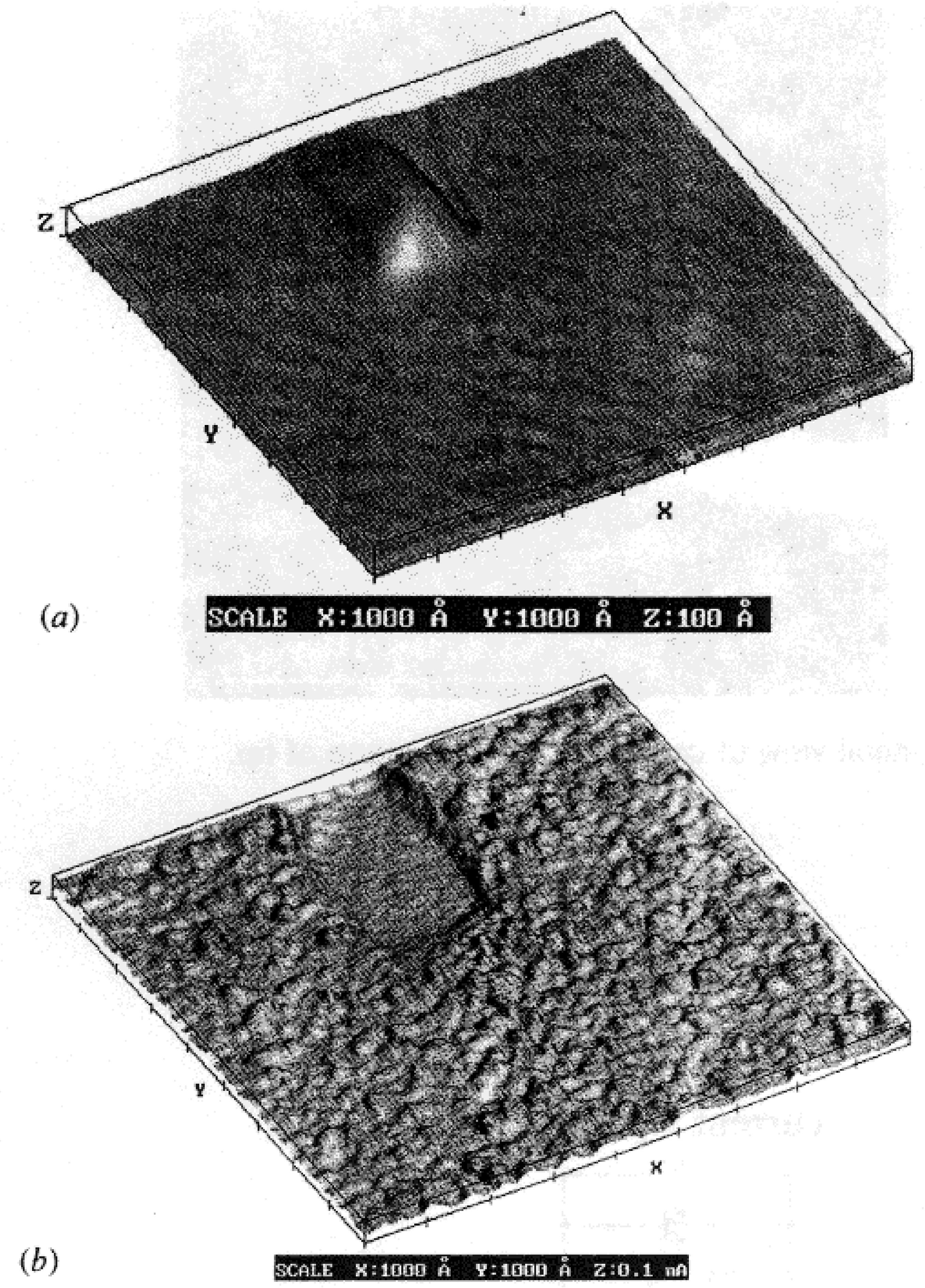

Figure 3. (*a*) The AFM image of the TiO_{2-x} film surface and (*b*) electrical conductivity image of TiO_{2-x} film surface.

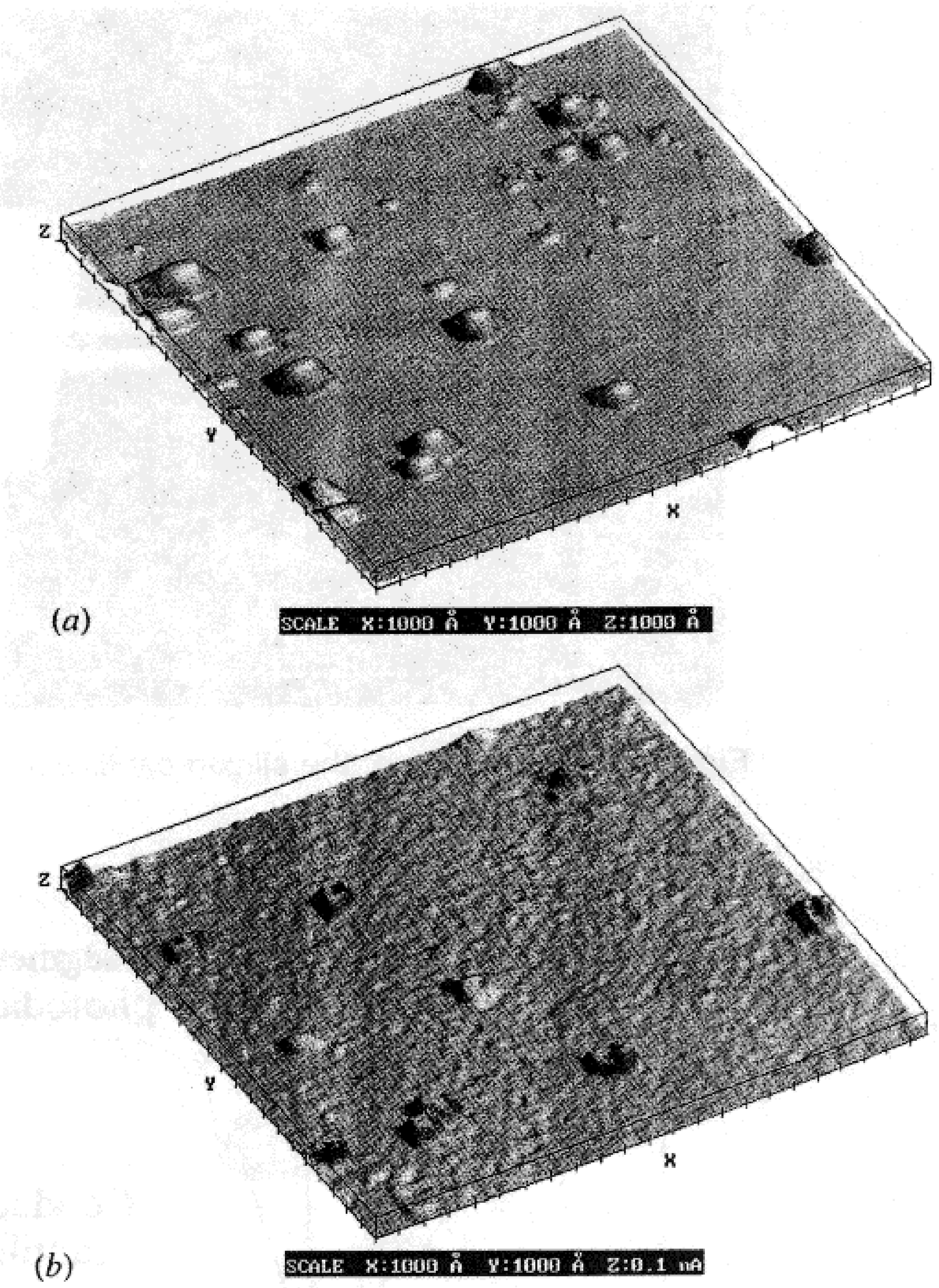

Figure 4. (*a*) The AFM image of the W_2C film surface subjected to special annealing at 900 °C and (*b*) electrical conductivity image of W_2C film surface.

3. Results and discussion

The surface resistance of W_2C, TiN and TiO_{2-x} films 1.5–10 nm thick was measured using the four-probe method. It was stated that films thicker than 1.5 nm are compact. The resistivity of these films was about 25, 100, and 180 $\mu\Omega$ cm, respectively. All films are characterized by enhanced adhesion to silicon. For example, the films are removed from the substrate at more than 500 g mm^{-2}. The films are chemically stable to alkalis and most acids (HF, HNO_3, HCl). SIMS analysis of the interface between the film and silicon substrate has shown the absence of a native oxide. In these cases we can reduce the thickness of the conductive coating, thus maintaining a small tip apex radius.

I–V analysis of the system 'conductive cantilever–test conductive surface (graphite)' has shown that the surface of the treated conductive films did not contain the native oxide. It follows from I–V measurements that the current in the system increases practically from zero voltages when the tip of the cantilever was placed under the test conducting surface in contact-mode AFM. After multiple scanning (~20 cycles) at the graphite surface by the same cantilever the current was still at the same fixed voltage. This indicates the high wear capability of the coatings.

It follows from the results of investigating silicon substrates formed on ultrathin (more than 1.5 nm) W_2C, TiN and TiO_{2-x} films by use of SECM that these films are also conductive and compact. The AFM image of the TiO_{2-x} film surface is shown in figure 3(*a*). The current density distribution on the same surface area is presented in figure 3(*b*). It can be seen that the homogeneous surface structure contains a non-conductive defect, probably an absorbed dielectric particle. The AFM image of the surface area of a W_2C film annealing at 900 °C is shown in figure 4(*a*). The distribution of the current density on the same surface area is presented in figure 4(*b*). It can be seen that the film surface included a drop-like phase. After high-temperature annealing the material of ultrathin amorphous films tends to form drops. Long thermal annealing thus results in the formation of non-conductive dispersed films.

4. Concluding remarks

It has been shown that ultrathin (1.5–10 nm) W_2C, TiN and TiO_{2-x} films can be used as coatings for conductive probes on silicon cantilevers. The films are characterized by high conductivity, increased adhesion to Si and chemical passivity. It has been shown by means of conductive SPM measurements that a dielectric layer is absent on the film surface and conductive metal-coated cantilevers are wear-proof.

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