Conductive indium nanowires deposited on silicon surface by dip-pen nanolithography

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Abstract. Conductive indium nanowires up to 50 nm in width and up to 10 µm in length are fabricated on the surface of silicon by local resputtering from the probe of an atomic-force microscope. To accomplish this, indium was transferred from an atomic force microscopy tip to the surface by applying a potential difference between the tip and substrate. The fabricated indium nanowires were several micrometers in length. Unlike thermal DPN, our DPN method hardly oxidized the indium, producing nanowires with conductivities from $5.7 \times 10^{-3}$ to $4 \times 10^{-2}$ Ω·cm.

1. Introduction

Dip-pen nanolithography (DPN)$^{1, 2}$ is a method by which metals or organic compounds can be directly deposited on a substrate from an atomic force microscopy (AFM) tip. This technique is useful in nanoelectronics as a way to fabricate conducting nanowires$^{3, 4}$ and in studying biomolecules and polymers in controlled locations$^{5-7}$. The DPN method makes possible the formation of conductive structures on semiconductor surfaces with a resolution of no worse than 50 nm. In thermal DPN, metal is transferred from an AFM probe onto the surface by heating the probe to the melting point of the loaded metal. Metals with low melting points such as indium, tin, and lead are required. When the metal on the probe tip is heated to its melting point, it transfers to the surface of the semiconductor by a metal–surface adhesion force. However, heating the metal oxidizes it, significantly reducing the conductivity of the fabricated nanostructures.$^1$ To reduce oxidation, in this paper, we deposited metal from an AFM probe by applying an electric potential between the tip and substrate.

2. Materials and methods

Indium (99.99%) was loaded onto the AFM probe tip by thermal vacuum spraying. To control the indium thickness, thermal spraying was performed through a mask with a hole of 6 µm diameter located 2 µm from the probe tip. To improve adhesion of indium to the probe, a layer of Ni and 30 nm of Cr were first deposited on the probe. Then, indium was deposited with a thickness from 80 to 200 nm (Figure 1a). Indium was deposited from the AFM tip onto the stepped surface of Si (111) with an interaction force of $10^{-7}$ N between the probe and the surface at room temperature. We fabricated structures with a vertical resolution of 0.2 nm on the smooth surface of Si (111) covered with 15 nm of anodic oxide as an isolation layer, matching our earlier study of local anodic oxidation$^9$ caused by AFM. A positive potential of 10 V was applied to the AFM cantilever, during which the indium-coated probe was moved parallel to the surface in lines for 1–2 µm at 0.1 µm/s.
3. Results and discussion

3.1. Nanowire formation

Using the indium-coated AFM tip, we fabricated several indium nanowires on the stepped surface of Si(111). After fabricating the nanowires, we investigated a section of each sample using AFM, which had a sharp tip with the radius of curvature of less than 10 nm. Figure 1b shows an AFM image of indium nanowires on the Si(111) surface. Analyzing the relief profile of the fabricated nanowires, we found their width to be 50–70 nm and their height to be 0.8–1 nm.

![Figure 1(a,b,c).](image)

(a) High-resolution transmission electron microscopy (HRTEM) image of the AFM probe coated with indium. The total volume of the coating is about 0.1 µm³. (a), (b) AFM topographic image of the surface of silicon with formed indium nanowires, (c) AFM image of area with connected contacts.

3.2. The mechanisms of nanowire formation

To establish the factors that influence the geometric dimensions of the resultant indium nanowires, during the transfer of indium, we varied the potential between the probe and the surface from 3 to 10 V and the force of interaction between the probe and the surface from $10^{-7}$ to $5 \times 10^{-6}$ N. It is found that the dependences of the height of the resultant structures on the applied potential between the probe and the surface and on the force of interaction between the probe and the surface are linear. This means that the nanowire height depends on both the applied potential and the force of interaction between the probe and the surface. It is conceived that the transfer of indium proceeds, on the one hand, due to a high-strength electric field (up to $10^8$ V cm$^{-1}$) formed in the region of the tip edge and, on the other hand, due to current flow between the substrate and the tip, with the local heating and melting of indium in the current channel. In this case, the application of voltage results in the reproducible resputtering of about 1% indium from the tip to the surface. At the same time, if the potential is not applied, the transfer of indium to the surface stops immediately after lubrication of the edge region (0.01%); in this case, the process sometimes does not occur, i.e., is irreproducible. The amount of transferred indium (~1% of the total coverage) can be attributed to localization of the high field at the very edge of the tip. 1% portion of the material is located within a region ~0.3 µm from the center. On the assumption that resputtering is initiated by an electric field, the critical-field strength at such a distance from the tip is $3 \times 10^5$ V cm$^{-1}$. Such a field is not high enough for molecules to dissociate. However, if the tip is pressed to the substrate, this field is high enough to activate the surface drift of indium from the tip to the substrate surface. In general, the physical nature of the transfer of indium from the tip to the surface in a high field with a current invites further investigation.

3.3. Nanowire electrical resistivity

To study the electrical properties of the resultant indium films, we fabricated two separated 10 nm thick gold contacts on an insulating substrate. The spacing between the contacts was no larger than 1–
2 µm. Then, using the method described above, we deposited indium onto the substrate region between the gold contacts (Figure 1c). As a result, the contacts were connected by an indium strip with a width of 0.3–1.3 µm and a height of 10–260 nm. Measurements show that the resistivity of the deposited indium corresponds to $5.7 \cdot 10^{-3} - 4 \cdot 10^{-2} \, \Omega \cdot \text{cm}$.

4. Conclusion
In summary, we developed a new DPN technique that allows one to fabricate indium nanowires with diameters of 30–50 nm on semiconductors and insulators. Unlike thermal DPN, our DPN technique does not require the AFM tip to be heated to indium’s melting point. Indium transport was possible because of local heating generated by electrical current from the AFM probe tip to the surface under positive potential. The main advantage of this technique is the high conductivity of the produced indium nanowires because of decreased indium oxidation. The measured indium electrical resistivity varied from $5.7 \cdot 10^{-3}$ to $4 \cdot 10^{-2} \, \Omega \cdot \text{cm}$.

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