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Electrochemical lithography: fabrication of nanoscale Si tips by porous anodization of Al/Si wafer†

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Porous anodization of Al/Si wafer in sulfuric acid results in the formation of Si nanotips on the surface of Si substrate with ultrahigh packing density.

Fabrication of nanoscale particles is mainly based on chemical methods,[1] however, as minimum feature sizes continue to decrease, fabrication reliability grows less certain. It remains difficult to scale down nanostructures to the few nanometers range in an efficient and parallel process in order to meet the requirement of the microelectronics industry.[2] Here we report a method, which may offer an alternative to achieving these goals and provide in principle the *in-situ* fabrication of Si nanotips on Si surface with ultrahigh packing density. This was carried out by using anodic porous alumina (APA) as a pattern-transferred nanomask for directional anodizing of a Si wafer. The method is referred to as electrochemical lithography (ECL). It is well known that acid-anodized aluminium forms amorphous alumina with long and columnar nanopores with approximately hexagonal ordering.[3] Perfect hexagonal ordering of these nanopores can be achieved now.[4] Although the Si nanostructural arrays produced on Si wafers by using APA films[5] and new pattern-transferred nanomask of APA with ultrasmall pore diameter of <10 nm have been reported,[6] the current work presents a much simple approach to produce the final structures.

The e-beam evaporated thin Al films (99.99%, thickness < 1 μm) on a Si substrate [Al/Si, Si: p-type, 0.5 Ω·cm, 5°-off (100)] were anodized in sulfuric acid (15 wt.%) under constant voltage (20 V dc) at room temperature (RT, 10 °C). By stopping anodization at certain points (Fig. 1), the samples of Al (sample A, indicated by the arrow A) and Si tips (samples B and C, indicated by the arrows B and C, respectively) were obtained which are timely monitored by *i–T* curve. The samples were investigated by transmission electron microscopy (TEM). TEM specimens were prepared by polishing and Ar ion milling (Gatan); HRTEM was performed using a JEM-4000EX (JEOL), and TEM in a JEM-200CX (JEOL). For clear viewing of the Si-tip arrays by atomic force microscopy (AFM), we also fabricated the sample of the Si tips by anodizing the same starting sample of Al/Si as that of the 20 V case under 40 V dc. Anodization in this case didn't stop until the APA film detached from the Si substrate. Subsequently, the content Al*x*O*y* within the SiAl*x*O*y* layer (Fig. 2b) and the remaining barrier layer (detached cell tips) were removed by wet chemical etching in a mixture of phosphoric acid (6 wt.%) and chromic acid (1.8 wt.%) at 60 °C, and oxidized Si (SiO*x*) below the pore base was removed by using deoxygenated HF (0.1 vol.%) at RT, the sample was dried in a vacuum box. AFM was performed immediately (NanoScope III, Digital Instruments).

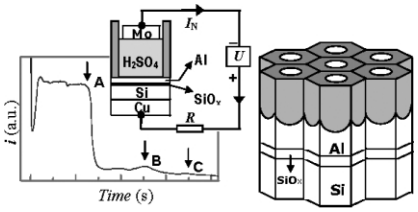

Fig. 1 Sketch of experimental setup for fabricating the Si tip (top) and classical model of the cellular structure (cell bundle) of a perfect APA film on Al/SiO*x*/Si (right). The arrows A, B and C in current density-time (*i–T*) curve (20 V dc) indicate three typical points of the sample in the process of anodizing. Native SiO*x* layer on Si developed due to air exposure before Al evaporation.

† Electronic supplementary information (ESI) available: Cartoon of tip formation and discussion on the sample anodising under 40 V dc. See http://www.rsc.org/suppdata/cc/b3/b315810a/

Fig. 2a shows the morphology of the Al-tip arrays within the APA/Al/SiO*x*/Si interfaces (sample A). During anodizing, the Al film has almost been completely oxidized at the point A (Fig. 1). The Al-tip arrays resulted from the close-packed cell tips due to field-assisted dissolution;[3] Shingubara *et al*. extended this concept and successfully made the Al nanodots.[7]

Fig. 2b reveals the formation of Si tips on the surface of a Si wafer (sample B). Therefore, the point B (Fig. 1) indicates the commencement of silicon oxidation[8] and the development of Si tips. Note the cell of APA film and the oxide below the pore base, which evidently indicated that the anodization of Al films on Si to form APA films can be continued after the Al film is consumed to anodize the Si wafer. We deduced that the formation of Si tips should result from counter-migration of Al^{3+} ions, Si vacancies and oxygen-containing anions under the high electric field across the interfaces of oxide/electrolyte and oxide/Si substrate (oxide growth front, Fig. 3). When the Al film was almost oxidized, the cell head was very close to the (APA+SiO*x*)/Si interface; the counter-migration across the pore bottom (the barrier layer) of the cell and the native SiO*x* layer would induce the oxidization of the Si

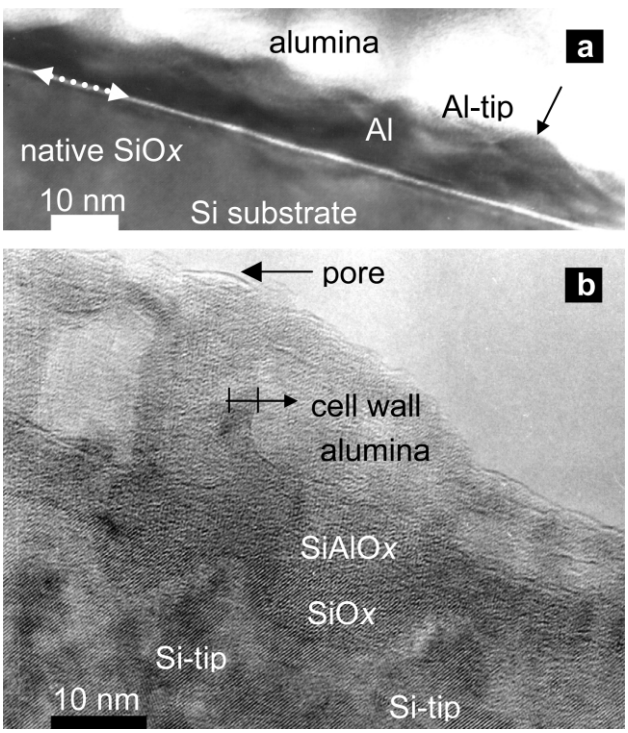

Fig. 2 Cross-sectional HRTEM images of (a) the Al and (b) Si-tips.

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substrate below the pore base. At the scalloped pore base, the electric field distribution is inhomogeneous both laterally and inward in the oxide.[4,9] Its depth dependence arises, first of all, from the non-planarity of the barrier layer and also from the space charge accumulated in the oxide during its growth. The lateral distribution of the electric field along the pore base surface is also inhomogeneous: the maximum electric field is concentrated at the pore center and decreases towards the pore walls. Therefore, oxide growth is also inhomogeneous at both internal and external oxide interfaces as a result of ionic species and vacancies movement. This results in preferential oxidation of the Si at the pore base while the Si under the APA pore walls is oxidized at a slower rate, thus it forms the Si tips neighboring to these SiAl*x*O*y* or SiO*x* islands below the pore base (Fig. 3b). That is, the Si tips by ECL are below the junctions of the boundaries of three‡ or more neighboring cells. The cell will cease to grow up after the Al film is consumed. After this time, the field-assisted dissolution of the barrier layer will reduce the thickness of the barrier layer (even remove the barrier layer completely if the anodising time is long enough). This enhances the counter-migration along the pore axes and oxidizes much Si below the pore base, and thus the Si-tips are sharpened (Fig. 4).

Fig. 5 shows an AFM image of the Si tips with a surface density of the tips of about 4×10^{10} cm^{-2} (40 V sample, see ESI †).

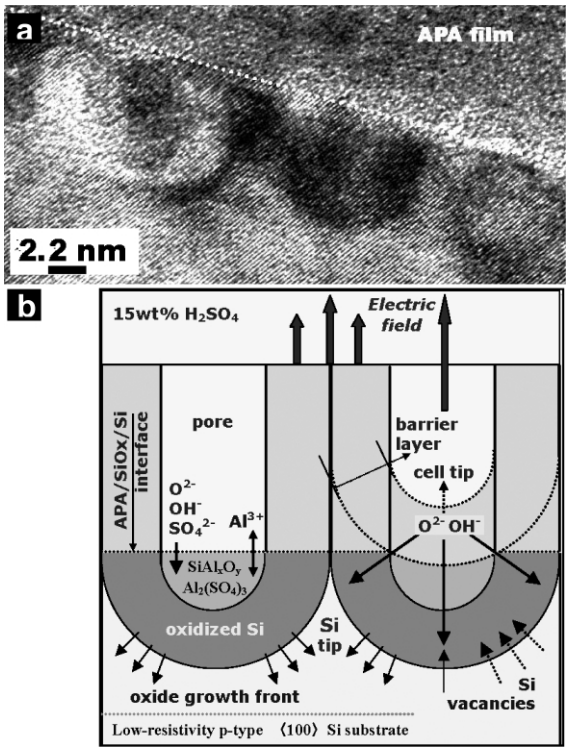

Fig. 3 (a) Cross-sectional HRTEM image of APA/SiO*x*/Si interfaces (sample B). (b) Sketch of the formation of the Si tips (see ESI †).

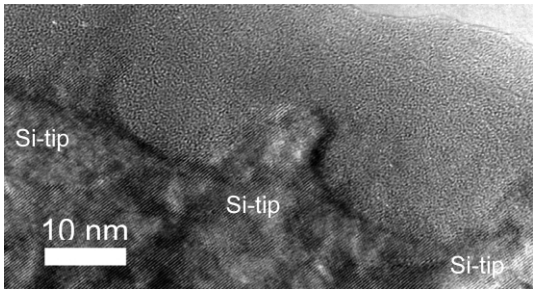

Fig. 4 Cross-sectional HRTEM image of SiO*x*/Si interface reveals that the Si tips were sharpened after 600 s anodizing (sample C, note Fig. 1).

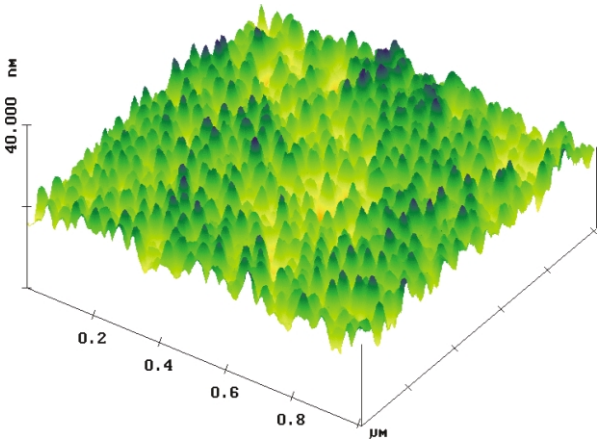

Fig. 5 Oblique AFM image of the Si tips with a partially ordered lattice (40 V sample).

In short, we fabricated the Si tips with ultrahigh packing density by ECL. The tip density is larger than the pore density of the mask (see ESI †), and every tip has the same crystal orientation as that of the starting wafer. Note that the success in fabrication of highly ordered APA film[4] should allow the tailoring of the Si-tip lattice in a controllable and practical way. Some other materials (InP,[10] Ti[11]), which form a porous structure during anodization, could also be used as substrates for ECL to make other material tips.

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Notes and references

‡ Location correlation between the Si tip and the cell of the APA mask: if using a highly ordered APA film[4] as the ECL mask, because of the hexagonal geometry of the pores, this number is *three* and should result in the formation of the ordered Si-tip lattice. However, in the current study, due to anodizing of the thin Al film, the cell lattice of the APA mask was partially ordered, and thus induced random Si tips (Fig. 5, see ESI †).

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