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Patterned aluminum nanowires produced by electron beam at the surfaces of AlF_3 single crystals

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Abstract

Cubic- and rectangular-shape single crystals of α-AlF_3 in sizes of 5–50 μm have been synthesized by a solid–vapor phase process. Using the electron beam induced decomposition of AlF_3, a method is demonstrated for fabricating patterned aluminum nanowires in AlF_3 substrate in a scanning electron microscope. By controlling the accelerating voltage, the beam current and scanning time, it is possible to fabricate metallic nanowires of different sizes. The aluminum nanowires may act as nano-interconnects for nanoelectronics. This work demonstrates a potential technique for e-beam nanofabrication.

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One-dimensional nanostructures have been extensively investigated in recent years due to their quantum properties and potential applications in materials research, opto-electronics, physics, chemistry, and biomedical science [1–3]. If one-dimensional nanostructures are to be used in large-scale commercial applications, then these novel structures must be aligned or patterned either during or post-synthesis. There are a few approaches that have been successfully demonstrated for aligning one-dimensional nanostructures through natural growth [4], pattern guided hydrofluid process [5], shadowed deposition of metals [6], or self-assembly through surface functionalization [7].

Direct electron beam writing for creating patterned one-dimensional nanowire structures is of great interest for applications in nanoelectronics. The objective of this paper is to demonstrate a novel approach or creating metallic nanowires in AlF_3 insulator substrate. It is known that aluminum trifluoride (AlF_3) is of potential applications as a catalyst in heterogeneous reactions [8]. It is also potentially useful as a resist [9] or storage material for atomic hydrogen [10]. The existing literature is mainly about polycrystalline films of AlF_3. In this paper, we first present a novel and simple technique for growing large-size AlF_3 single crystals. Then, the AlF_3 crystals are used for creating metallic aluminum nanowires using a fine electron beam in a scanning electron microscope. This technique provides a possible approach for developing complex metallic patterns by electron beam.

The AlF_3 films prepared by chemical method are mostly rough at the surface and have a polycrystalline structure [11]. The first task of our study is to synthesize single crystalline AlF_3. Our approach is based on a solid–vapor phase process used for synthesis of nanobelts [12]. Synthesis of AlF_3 was based on a thermal evaporation of commercial grade AlF_3 (purity: 99.5%) powder under controlled conditions (Fig. 1). The powder was placed in the center of a tube furnace and evacuated for several hours to a pressure of $\sim 10^{-2}$ mbar in order to purge the oxygen in the system. After evacuation, the temperature of the system was raised to 1350 °C at a rate of 15 °C min^{-1} and held there at a

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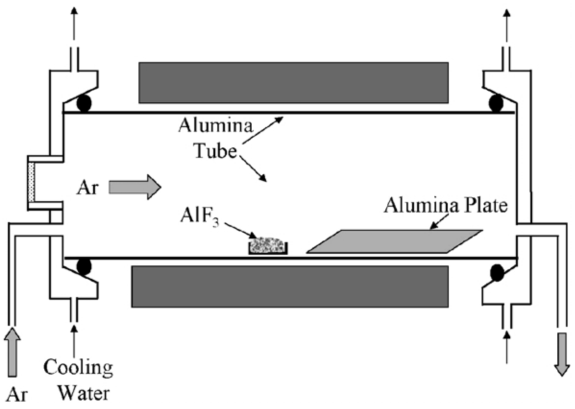

Fig. 1. Schematic of the tube furnace apparatus for the synthesis of single crystal AlF_3.

constant pressure of 300 mbar for 1–2 h. A steady flow of argon gas was sent through the tube at a rate of 50 sccm, which acted as a carrier gas to transport the AlF_3 vapor to cooler temperature regions, where it might deposit onto alumina plates located downstream from the source material. The as-deposited material was characterized and analyzed by X-ray diffraction (XRD: Philips PW 1800 with Cu Kα radiation) and scanning electron microscopy (SEM: LEO 1530 FEG).

Since AlF_3 has several phases, it is essential to determine the phase of the as-produced AlF_3 by XRD [13]. An examination of the sample with XRD indicates that it has a rhombohedral crystal structure with space group $\bar{R}3(148)$ (Fig. 2). This corresponds to the α-AlF_3 structure, the most stable form of aluminum trifluoride. The peaks in the XRD pattern are in good agreement with the standard data for α-AlF_3 (JCPDS No. 44-0231). The sample is pure and without the presence of other phases.

SEM images reveal the well-faceted morphology of the as-deposited material (see Fig. 3). These results differ from the morphology previously reported by other groups who have synthesized α-AlF_3 through plasma-assisted

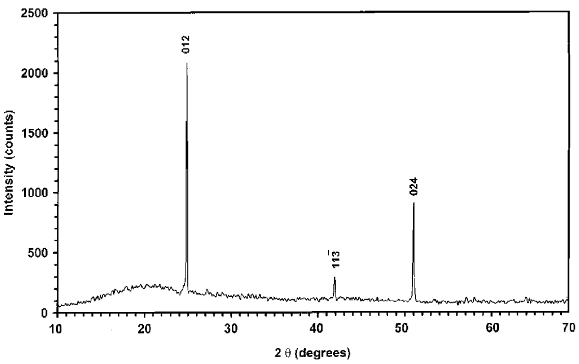

Fig. 2. XRD pattern recorded from the as-produced AlF_3.

fluorination reaction with nitrogen trifluoride [11] and thermal decomposition of hexafluoroaluminate [13]. In those studies, porous α-AlF_3 was synthesized and the surface morphology is rather rough. With our technique, a cube or rectangular shape has been produced, which is single crystal and with flat surfaces. To the best of our knowledge, this is the first demonstration of the well-faceted α-AlF_3 structure that is suitable for electron beam fabrication of nanostructures. Dimensionality of the cubes and rectangles can be tailored by controlling synthesis temperature and deposition time, and their sizes range from 5 to 50 μm. In general, material collected further away from the source had finer features than those collected near the source material, i.e. higher temperature region and higher concentration of AlF_3 vapor are the major factors in controlling dimensionality.

AlF_3 is very sensitive to electron beam illumination, and the structural transformation occurs very quickly under the beam, thus, the application of transmission electron microscopy to this material is limited. Wang and Cowley [14] used AlF_3 to produce metallic nanoparticles by electron beam illumination in TEM. Chen et al. [15] used electron beam to induce structural transformation from amorphous AlF_3 to crystallized α-AlF_3. Saifullah et al. [16] studied the effects of electron beam on FeF_3. A consequence of electron beam illumination is to transform AlF_3 into Al due to the radiation damage of the beam, resulting in the release of the F^- ions from the lattice. By using the electron beam in an SEM, we may be able to produce patterned lines of aluminum in the well-faceted AlF_3 crystals. Instead of illuminating the entire sample with the electron beam, we made only line scans. A schematic representation of the fabrication process of the aluminum nanowires is given in Fig. 4(a). From the SEM images (Fig. 4(b) and (c)) acquired prior and post illumination by an electron beam, it is apparent that line features have been created by the electron beam, as shown by the arrowheads in Fig. 4(d). The most important thing is that the nanowires are created only at the area scanned by the electron beam, provided the scanning time is long enough.

To induce the transformation from AlF_3 to Al in the sample, an accelerating voltage of 14 kV was used for a scanning period of 1–5 min. Line scans of varying voltages at different time scales were methodically conducted on an α-AlF_3 crystal in order to determine the parameter ranges that produced Al nanowires (see Fig. 5). Beginning with low accelerating voltage, a 1 kV incremental step at a constant scanning time of 3 min were used to determine the minimum voltage required to volatilize the F^- atoms. Our observations revealed that 12 kV had sufficient energy to produce an aluminum nanowires. Increasing the scanning time of the electron beam from 3 to 7 min made the Al nanowires more visible. This is expected since a longer scanning time results in more F_2 gas being evolved.

The aluminum nanowires are formed due to the electron beam induced decomposition following $AlF_3 \rightarrow$

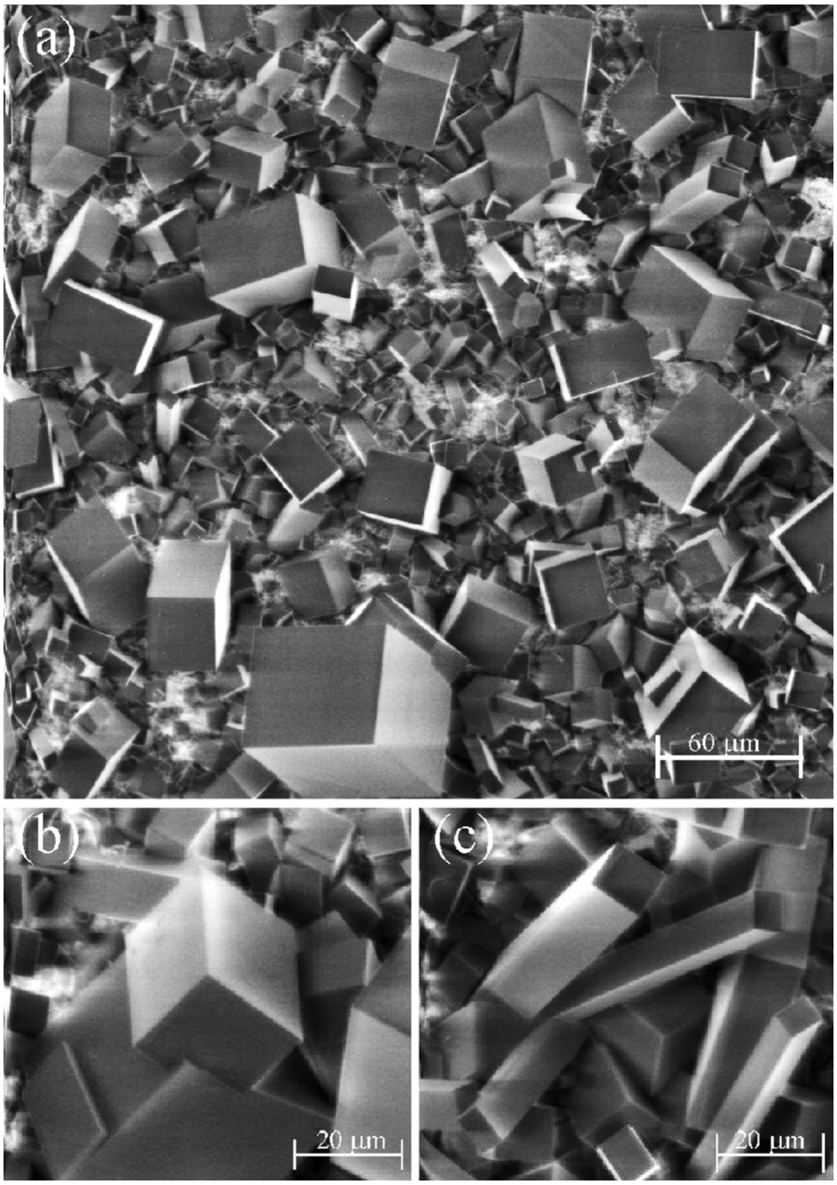

Fig. 3. SEM images of the α-AlF_3 at low magnification. Images (a) and (b) depict the well-faceted cube morphology, while image (c) depicts the well-faceted rectangular morphology collected from a higher temperature region.

$Al + 3/2F_2$. The size of the Al nanowires produced by the electron beam is determined by the voltage, scanning time (or illumination dosage) and the probe size. Manipulating these parameters could produce different sizes of nanowires, as shown in Fig. 5. It is apparent that the scan time affects the line width and the operation voltage can also affect the line width. The data demonstrate that the technique allows, in principle, size-controlled fabrication of nanowires in specified lengths at specified locations.

In summary, single crystal cubic-shape AlF_3 has been synthesized by a solid–vapor phase process. A method is demonstrated for fabricating patterned aluminum nanowires in AlF_3 using the electron beam in SEM. Since AlF_3 is electrically insulating, the aluminum nanowires may act as nano-interconnects for nanoelectronics. By controlling the accelerating voltage, the beam current and scanning time, it is possible to fabricate metallic nanowires of different sizes. This demonstrates a potential technique for e-beam nanofabrication.

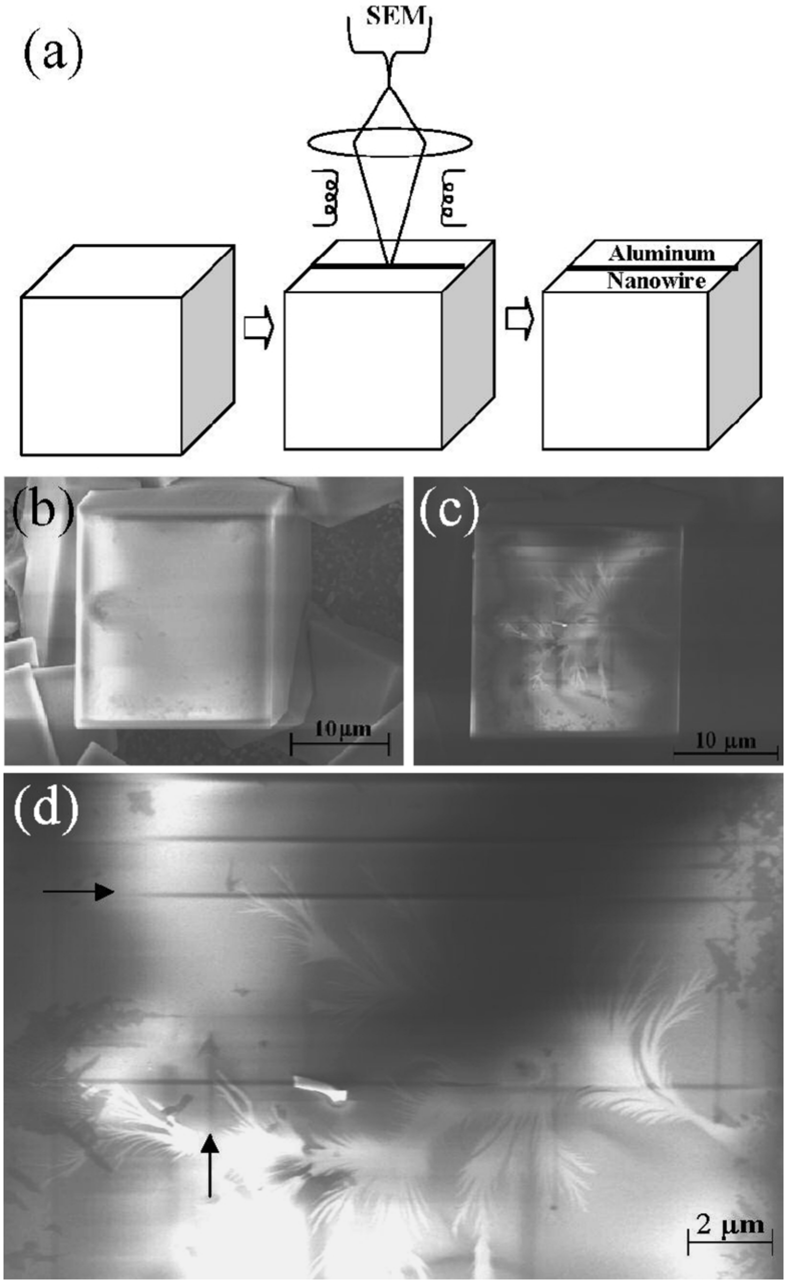

Fig. 4. (a) Schematic of process used to fabricate patterned Al nanowires. (b,c) SEM images of the α-AlF_3 crystal before and after scanning by the electron beam along the lines, respectively, showing the formation of nanowires along the beam scanning direction. (d) High magnification SEM image of the cube after it has been scanned by an electron beam. The background feature is produced by the discharge of the substrate during SEM imaging. The beam energy used for the writing was 14 kV.

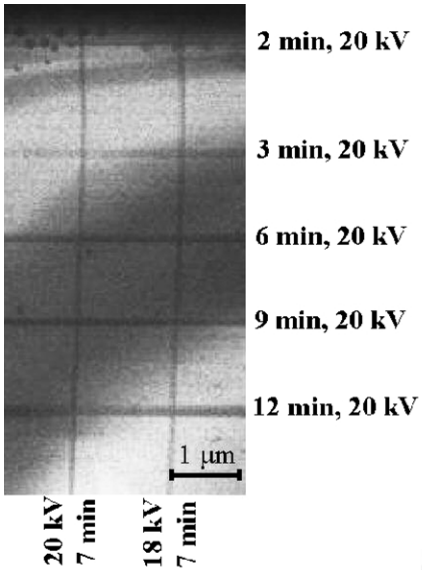

Fig. 5. SEM image of nano-interconnects produced on an α-AlF_3 substrate under different experimental conditions, showing the possibility of controlling line width by scanning time.

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