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Oriented growth of magnesium nanowires by physical vapor deposition in high vacuum

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ABSTRACT

[11−20]-oriented magnesium nanowires were prepared at 703 K for 30 min in a high vacuum level of 10^{-4} Pa by physical vapor deposition method. The evaporation temperature and vacuum level are the two key factors in the preparation of the magnesium nanowires. A growth mechanism that the magnesium nanowires prefer to grow in the closest packed direction, which has the largest binding strength, is proposed to explain the oriented growth of the magnesium nanowires.

Mg nanowires have exhibited some exciting advantages in the applications of new energy materials field. For example, in the field of hydrogen storage materials, magnesium is regarded as the most potential material with the hydrogen absorption capacity of 7.6 wt.%, and the Mg nanowires with the diameter of 30–50 nm have a higher hydrogen absorption capacity and faster hydrogen absorption/desorption kinetics than the Mg nanowires with the diameter of 150–170 nm [1]. Also in the field of electrochemical storage and generation of energy in batteries, Mg/air battery system has shown the advantages of a high theoretical voltage and energy density, low cost, light weight and environmental friendliness, and the current densities of the electrodes made from Mg nanostructures (nanorods or sea-urchin-like nanostructures) are much higher than that of the electrode made from commercial Mg powder [2]. In the preparation of Mg nanostructures, several physical vapor deposition methods, such as vapor transport [1,2], sputtering [3] and oblique angle deposition [4–7], have been reported. However, the formation mechanism of Mg nanostructure, especially the Mg nanowires, is still unclear. So it is very necessary to carry out the research on this issue.

As one of the most efficient methods in the preparation of nanomaterials, physical vapor deposition has received more and more attentions in recent years. It has been used to prepare Sn nanowires [8], Zn nanowires [9], Cu nanowhiskers [10], etc. In the preparation of Sn nanowires, Sn vapors were transported to the Si(100) substrates in the cooler region by a nitrogen gas flow, and condensed to form Sn nanowires and nanosquares at deposition temperatures of 483 K and 453 K, respectively. In the preparation of Zn nanowires, a cold-wall physical vapor deposition chamber was used, in which the deposition temperature was controlled at 423 K for the growth of wool-like nanowires. It can be seen that the deposition temperature played an important role in the preparation of nanowires. In the preparation of Cu nanowhiskers, it was found that a high deposition temperature ($0.65T_m$ of Cu) was necessary to achieve nanowhisker growth, which is thought to be related to high atom diffusivity and moderate supersaturation. Thus in the present work a deposition temperature approaching 703 K, which is $0.65T_m$ of magnesium, is used to prepare the magnesium nanowires.

Commercial pure Mg powders (purity > 99.9%) were poured into a stainless steel container to produce evaporation. A piece of stainless steel mesh (1500 counts in an area of 2.54 cm × 2.54 cm) was covered on the top of the stainless steel container and was used as a substrate for the deposition of Mg. Both the stainless steel container and the mesh were placed in a quartz tube. The quartz tube was then placed in a furnace and connected to a molecular pump. A high vacuum level of 10^{-4} Pa was used during the process of evaporation and deposition. The temperature and time for the evaporation and deposition of Mg powders was 703 K and 30 min, respectively. After cooling to room temperature, the

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as-prepared products were examined by scanning electron microscopy (SEM), X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM).

On the surface facing the evaporation source, a layer of white materials is observed by the naked eye, while on the other surface nothing is visible. The white materials were further examined by SEM. It can be seen from Fig. 1 that lots of nanowires and nanoparticles are found on the surface of the steel wires, among which the nanoparticles are distributed homogeneously on the surface of the steel wires, while the nanowires tend to be concentrated at the intersection of the steel wires. The nanoparticles have the shape of irregular polyhedrons, while the nanowires are in the shape of needle-like crystals growing bolt upright out of the surface of the steel wires. The XRD result shows that these nanowires and nanoparticles are magnesium, as expected. (The other two strong peaks are from the steel wires of austenite Fe.) The dimensions of these nanowires were determined by statistical methods. Two hundred nanowires were sampled. The results indicate that the length of these nanowires is most frequently about 1.25 μm and the diameter is most frequently about 75 nm.

In order to identify the growth orientation of the Mg nanowires, TEM work was carried out. The results are shown in Fig. 2, where it can be seen that the nanowire is in the needle-like shape and grows in a particular direction. It reveals that the crystal plane with an interplanar spacing of 0.28 nm (mark B in Fig. 2) is the $(10-10)$ plane of Mg crystal ($d_{(10-10)}$ = 2.7789 Å) and that the crystal plane with an interplanar spacing of 0.16 nm (mark C Fig. 2) is the $(11-20)$ plane of Mg crystal ($d_{(11-20)}$ = 1.6044 Å). It also reveals that the side surface of the nanowire, which is indicated by a dashed line, is parallel to the $(10-10)$ plane and perpendicular to the $(11-20)$ plane. This means that the growth direction of the nanowire is along the $[11-20]$ direction, which is exactly the closest packed direction of the Mg crystal.

We believe that the theory proposed by A. Bravais and later modified by Donnay and Harker [11] can be used to explain the orientation of the growth of Mg nanowires in our experiment. The theory concerns the law of crystal growth morphology and its structure. In this theory, the crystal planes with higher reticular densities (the number of lattice points per unit surface) tend to grow more slowly than the crystal planes with lower reticular densities, and the crystallographic planes with high growth rates always tend to disappear in the crystal growth and the remaining planes are always those with low growth rates. Generally, a crystal plane with a higher reticular density has larger interplanar spacing. The crystal planes and interplanar spacing of Mg are shown in Fig. 3. It can be seen that the interplanar spacing of the $(11-20)$ plane is smaller than that of the (0001) plane and the $(10-10)$ plane; thus the growth rate of the $[11-20]$ direction is higher than that of the $[0001]$ and $[10-10]$ directions. As a result, these nanowires tend to grow along the $[11-20]$ direction rather than the $[0001]$ or $[10-10]$ directions.

The driving force for the fast growth along the $[11-20]$ direction is related to the smallest distance between the atoms in this direction. During the solidification from gas atoms to solid atoms, attachment energy, which acts as an energy trap to collect gas atoms, is needed. The attachment energy is decided by the binding strength between atoms. As is well known, the binding strength is a decreasing function of the bond distance: the smaller the distance, the larger the binding strength [12]. As shown in Fig. 3, the bond distance in the $[11-20]$ direction is less than that in the $[10-10]$ and $[0001]$ directions. Thus the binding strength in the $[11-20]$ direction is larger than that in the $[10-10]$ and $[0001]$ directions, leading to a fast growth in the $[11-20]$ direction.

In the formation of Mg nanowires, the temperature and vacuum level are found the two key factors. Based on our observation, a specific Mg vapor concentration is needed for the Mg nanowire growth. When the temperature was below 683 K, no Mg vapors were released and no products were obtained, while when the temperature is above 743 K, too many Mg vapors were provided leading to the formation of Mg nanoparticles rather than Mg nanowires. Moreover, when the vacuum level dropped from 10^{-4} Pa to

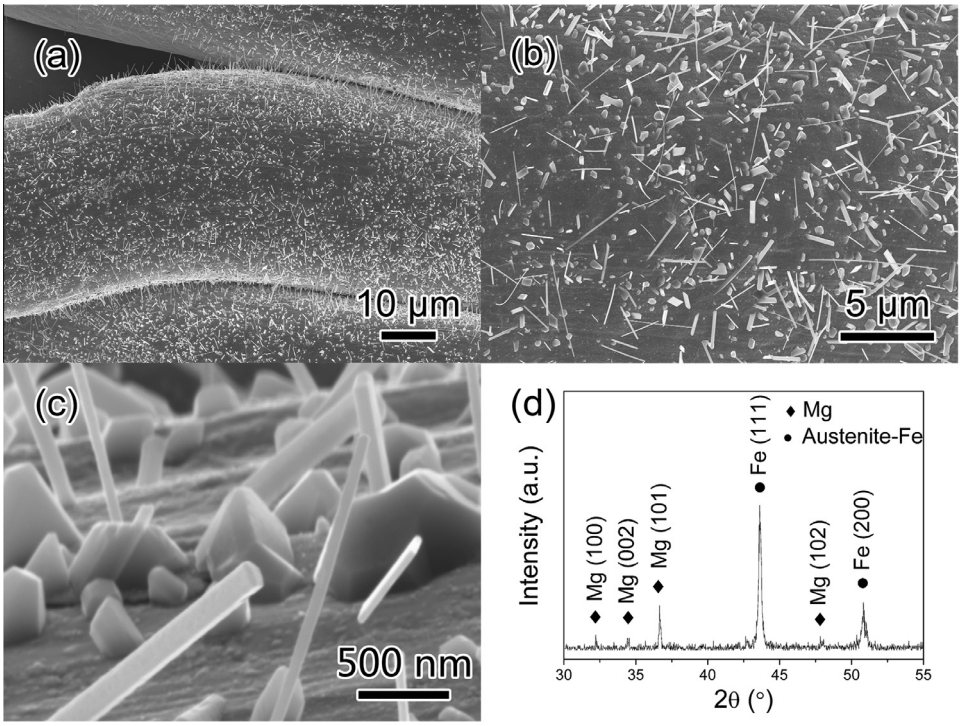

Fig. 1. SEM images of the magnesium nanowires: (a–c) SEM images with different magnifications, (d) XRD patterns of the magnesium nanowires on the stainless steel mesh.