Synthesis and Characterization of ZnO Bicrystalline Nanosheets Grown via Ag-Au Alloy Catalyst

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(Dated: Received on March 4, 2014; Accepted on April 11, 2014)

ZnO bicrystalline nanosheets have been synthesized by using Ag$_x$Au$_{1-x}$ alloy catalyst via the vapor transport and condensation method at 650 °C. High resolution transmission electron microscopy characterization reveals a twin boundary with {01-13} plane existing in the bicrystalline. A series of control experiments show that both Ag$_x$Au$_{1-x}$ alloy catalyst and high supersaturation of Zn vapor are prerequisites for the formation of ZnO bicrystalline nanosheet. Moreover, it is found that the density of ZnO bicrystalline nanosheets can be tuned through varying the ratio of Ag to Au in the alloy catalyst. The result demonstrates that new complicated nanostructures can be produced controllably with appropriate alloy catalyst.

Key words: ZnO, Bicrystalline, Nanosheet, Alloy catalyst

I. INTRODUCTION

ZnO, as a wide-gap (≈3.4 eV at room temperature) semiconductor with large exciton binding energy (60 meV), has widely potential applications for laser [1], field effect transistors [2], chemical and biological sensing [3], light-emitting devices [4], piezotronics [5, 6], solar cells [7], spintronics [8, 9], and transparent and flexible electronics [10]. Numerous ZnO nanostructures have been synthesized, such as ZnO nanorods [11], nanowires [12], nanocombs [13], nanobelts [14], nanosheets [15], and nanohelices [16]. Among the variety of methods for growth of ZnO nanostructures, vapor-liquid-solid (VLS) process via using metal particles catalyst is an important and facile method, and there have been reports on using Au [17], Sn [11], Ni [18], Cu [19], and Ag [15] as the catalyst. Obviously, different metal particles possess distinguishing features, which can result in different morphologies and properties of the synthesized ZnO nanostructures. For example, Au catalyst can generally produce one-dimensional ZnO nanowire and nanorod [17] whereas Ag catalyst often induces two-dimensional ZnO nanostructures [15]. On the other hand, the use of alloy catalyst can supply more choices and tricks to synthesize more complex and advanced nanostructures, gain more attention recently. An interesting example is that Ag-Au alloy can induce twin defects in Ge nanowires [20]. Although there are inspiring achievements ahead, to the best of our knowledge, synthesis of ZnO nanostructures with alloy catalyst has not been reported.

In this work, we report the ZnO bicrystalline nanosheets with twin defects can be synthesized with Ag$_x$Au$_{1-x}$ alloy as the catalyst. The systematic control experiment demonstrates that the Ag$_x$Au$_{1-x}$ alloy catalyst plays a key role in the formation of ZnO bicrystalline nanosheets through lowering the formation energy of the twinning defect of wurtzite ZnO. Our result supplies more insight into the defect engineering of the nanostructure by using the alloy catalyst.

II. EXPERIMENTS

The ZnO nanosheets were synthesized via a vapor transport and condensation method catalyzed by Ag$_x$Au$_{1-x}$ alloy catalyst in a two-heating-zone furnace. The experimental setup is schematically shown in Fig.1. Uniform mixtures (1:1 molar ratio) of ZnO powder (purity ≈99.99%) and spectrograde graphite powder were located at high temperature (HT) zone of the furnace in sealed end of a small quartz tube with the length of 27 cm and the inner diameter of 1.5 cm, whereas a Si(111) substrate coated by Ag$_x$Au$_{1-x}$ alloy catalyst was located at low temperature (LT) zone of the furnace in open end of the tube with the distance of 22 cm from the mixtures of ZnO and graphite. Ar (20 sccm) was used as the carrier gas in the whole reaction. The LT zone was heated up to 650 °C in 8 min, and then HT zone was heated up to 1000 °C in 40 min. Once the temperature of HT zone reached 1000 °C, O$_2$ (10 sccm) was introduced for 10 min, then the heat power of two-zone furnace and O$_2$ flow were shut down. The furnace...
FIG. 1 The schematic diagram of setup for preparation of ZnO nanostructures.

FIG. 2 (a) SEM image and (b) EDS of Ag$_{0.5}$Au$_{0.5}$ alloy nanoparticles on the Si(111) substrate. was cooled down to room temperature naturally under Ar gas protection.

The morphologies of the ZnO nanostructures and Ag$_x$Au$_{1-x}$ alloy catalyst were observed by JEOL-6700 field-emission scanning electron microscope (FE-SEM). The crystallographic information was revealed by a PHILIPS X’PERT PRO X-ray diffractometer (XRD) with Cu Kα line ($\lambda=1.54184$ Å). The microstructure information and energy dispersive X-ray spectrum (EDS) of the twinning ZnO nanosheets were characterized with JEM-ARM200F transmission electron microscopy (TEM) operated at 200 kV.

III. RESULTS AND DISCUSSION

The Ag$_x$Au$_{1-x}$ alloy catalyst is synthesized through sequential deposition of Ag (purity $\sim$99.99%) and Au (purity $\sim$99.99%) thin films onto the 10 mm$\times$5 mm$\times$0.5 mm Si(111) substrates via thermal evaporation and then annealed at 850 ºC for 20 min. The composition of the alloy can be readily controlled with the thickness ratio of two different metal films. Figure 2(a) is a typical SEM image of nominal Ag$_{0.5}$Au$_{0.5}$ alloy (prepared with 5-nm-thick Ag film and 5-nm-thick Au film) catalyst. As seen, the alloy film shows particle morphology and has a size distribution ranging from a few nanometers to about fifty nanometers resulting from the Ostwald ripening. The EDS result of Ag$_{0.5}$Au$_{0.5}$ alloy in Fig.2(b) demonstrates that the Ag/Au atomic ratio is about 0.4:0.6.

SEM image of ZnO nanosheets obtained with Ag$_{0.5}$Au$_{0.5}$ alloy catalyst is shown in Fig.3(a). The ZnO nanosheets have a typical length of tens of micrometers and width of several micrometers. Inset of Fig.3(a) clearly shows a groove -like morphology in the middle of nanosheet. The XRD result shown in Fig.3(b) indicates that the structure of sample is wurtzite ZnO (PDF 89-0511) with lattice constants $a=3.251$ Å and $c=5.205$ Å. The weak peak at 28.4º identified as (111) of single crystalline silicon (PDF 076268) comes from the substrate, while the peaks at 38.2º and 44.4º are identified as (111) and (200) of Ag$_{0.5}$Au$_{0.5}$ alloy (PDF 89-3697) respectively. On the contrary to the conventional VLS growth using metal catalyst, where the ZnO nanorods arrays are frequently perpendicular to the substrate, the nanosheets grown with the alloy catalyst are distributed randomly on the substrate, resulting in many diffraction peaks of wurtzite ZnO in Fig.3(b).

FIG. 3 (a) SEM image and magnified SEM image of ZnO nanosheets (the scale bar in the inset is 1 µm). (b) XRD result of ZnO nanosheets obtained with Ag$_{0.5}$Au$_{0.5}$ alloy catalyst.

DOI:10.1063/1674-0068/27/03/350-354 ©2014 Chinese Physical Society
TEM characterization is carried out to investigate the microstructure of ZnO nanosheets. Figure 4(a) is the TEM image of a typical ZnO nanosheet. Apparently, no Ag-Au particle can be observed on the ZnO nanosheet. Moreover, neither Au nor Ag signal can be found in the EDS results (not shown here) respectively collected from four random areas of the nanosheet. Figure 4(b) is a high-resolution TEM image taken from the groove-like area of the ZnO nanosheet and the two insets are corresponding selected area electron diffraction (SAED) patterns taken along the [2-1-10] zone axis of each side of the nanosheet (excluding the groove-like area). The image clearly shows that the groove-like region seen in Fig.4(a) includes a twin boundary. The fringe spacing of 0.52 nm can be indexed to the {0001} reflections of wurtzite ZnO. The SAED pattern taken from the circle area of Fig.4(b) is shown in Fig.4(c). As seen, two sets of spots can be distinguished, which are outlined with dashed-line and solid-line rectangles, respectively. The common spot is from the twin plane (01-13), as indexed in the SAED pattern. The two regions separated by the twin boundary are bicrystalline by a mirror operation on {01-13}. The angle between the two (0001) directions of ZnO bicrystalline nanosheet is estimated to be 117°, which is well consistent with the calculated datum of 116° in an ideal ZnO twin structure [21]. According to the above results, the structure of ZnO bicrystalline nanosheets can be schematically depicted in Fig.4(d). The fact that the twin plane (01-13) is parallel to the fast growth direction of the ZnO bicrystalline nanosheet implies the possible mechanism of defect induced crystal growth.

In order to understand the role of alloy catalyst in the synthesis of ZnO bicrystalline nanosheets, the control experiments using the pure Au (or Ag) metal catalyst were performed. The metal catalyst is fabricated with 10 nm Au (or Ag) film through the same annealing process as for the preparation of the alloy one. Figure 5 (a) and (b) show the SEM images of nanostructures obtained with Au and Ag catalyst, respectively, in which no bicrystalline nanosheet can be observed. As seen in Fig.5(a), the ZnO nanocombs can be produced with Au catalyst, due to the large supersaturation of Zn vapor [22]. Additionally, the failure of formation of ZnO nanosheets with Ag catalyst in our case can be attributed to that the Ag catalyst has to be used in a narrow temperature window around 475 °C and would lose the catalyst ability in the crystal growth for the temperature above 500 °C [15]. Therefore, we conclude that the AgₓAu₁₋ₓ alloy catalyst is prerequisite to synthesize the ZnO bicrystalline nanosheets.

We also carry out the synthesis of ZnO bicrystalline nanosheets using alloy catalyst with different Ag/Au ratios. Figure 5 (c) and (d) shows the produced ZnO bicrystalline nanosheets with nominal AuₓAg₀.₃₃ alloy catalysts. The scale bars in inset of (c) and (d) are 5 µm.
ZnO bicrystalline nanosheets with Ag$_x$Au$_{1-x}$ alloy catalyst. This implies that the formation of bicrystalline nanosheets is possibly related to other mechanism except VLS. Note that (01-13) twin boundary occurs in our case, which has also been observed in the previous reported ZnO nanostructures [23–26]. Therefore, it is reasonable to consider that the formation of twin nanostructures originates from a twin core in the nucleation stage of the crystal growth, which probably comes from the gas phase nucleation [27] according to vapor-solid (VS) mechanism [28]. In the VS process for preparation of ZnO nanostructure, the nucleation core of ZnO is created through the oxidation process of Zn clusters formed in the supersaturation of Zn vapor. Intuitively, the structure of nucleation core depends on both the catalyst and the supersaturation of Zn vapor. In this regards, we have to investigate the role of the supersaturation of Zn vapor. In our experiment, Zn vapor is firstly formed in the HT zone by carbon thermal reduction reaction, and then transported to the LT zone. The degree of supersaturation of Zn vapor in the LT zone can be well controlled by the accumulation time before the oxygen is introduced.

Figure 6(a) shows the SEM image of ZnO nanostructures obtained in the low supersaturation of Zn vapor with Ag$_{0.5}$Au$_{0.5}$ alloy catalyst. As seen, only ZnO nanorods can be found. The result indicates that the high supersaturation of Zn vapor is necessary to produce ZnO bicrystalline nanosheets. Once again, we note that, without Ag$_x$Au$_{1-x}$ alloy catalyst, the bicrystalline nanosheets cannot be formed even under the high supersaturation of Zn vapor, as seen in Fig.6(b). Therefore, we suggest that both Ag$_x$Au$_{1-x}$ alloy catalyst and high supersaturation of Zn vapor are crucial to the formation of ZnO bicrystalline nanosheets.

Considering the fact that twin boundary is a stacking fault defect, the possibility of creating a twin core relies on its formation energy. The result of Fig.6(b) shows the temperature of 650 °C is not high enough to overcome the thermodynamic barrier for the formation of the twin core in the absence of Ag$_x$Au$_{1-x}$ alloy catalyst, consistent with the previous report that the wurtzite ZnO bicrystalline nanobelts occurred only above the temperature of 950 °C [23]. Therefore, the successful synthesis of bicrystalline ZnO at low temperature of 650 °C with the Ag$_x$Au$_{1-x}$ alloy catalysts implies that the alloy catalyst can lower the formation energy of stacking fault of wurtzite ZnO. The results demonstrate that the alloy catalyst is an important strategy to control the nucleation and morphology of nanostructures.

IV. CONCLUSION

The ZnO bicrystalline nanosheets with (01-13) twin plane have been synthesized by using Ag$_x$Au$_{1-x}$ alloy catalyst. A series of control experiments show that both Ag$_x$Au$_{1-x}$ alloy catalyst and high supersaturation of Zn vapor are prerequisites for the formation of ZnO bicrystalline nanosheets. Moreover, we find that the density of ZnO bicrystalline nanosheets can be controlled through varying the Ag/Au ratio of alloy catalyst; the richer the Ag content, the higher density the bicrystalline nanosheets. Compared to the previous reports of bicrystalline produced under the high temperature, the bicrystalline nanostructure can be synthesized with mild condition in this work. This is owing to the decrease of twinning defect formation energy of wurtzite ZnO by the alloy catalyst. The result provides more insight into the preparation of new complicated nanostructures through the alloy catalyst.

V. ACKNOWLEDGMENTS

This work was supported by the Ministry of Science and Technology of China of China (No.2011CB921403), the National Natural Science Foundation of China (No.11374274 and No.11074231), and Chinese Academy of Sciences (No.XDB01020000).


