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Growth behavior and photoluminescence properties of ZnO nanowires on gold nano-particle coated Si surfaces

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ABSTRACT

ZnO nanowires arrays were synthesized on gold coated Si by the hydrothermal technique. The density of the ZnO nanowires array is found to be inversely proportional to the particle size of gold films. The initial nucleation of ZnO nanowires is found to nucleate at the boundaries of the gold nano-particle films. The density of the ZnO nanowires can be controlled through the particle size of the gold nano-particle films. Anomalous photoluminescence properties were observed from the as-grown ZnO nanowires.

1. Introduction

Nanoscale one-dimensional (1D) semiconductor materials have attracted great attention not only due to their fundamental importance but also due to the technological necessity [1]. Among them, ZnO nanowires have been extensively studied due to its interesting physical properties [2,3] and broad applications such as light emitting diodes [4], room temperature lasers [5], ultraviolet (UV) detectors [6], field-emission displays [7], solar cells [8], and piezonanogenerators [9]. Various methods have been adopted to synthesize ZnO nanowires, such as metal-organic chemical vapor deposition (MOCVD) [10], electro-deposition [11], vapor–liquid–solid (VLS) epitaxy [12], pulsed laser deposition (PLD) [13], etc. In comparison, hydrothermal synthesis is the easiest technique for fabricating the ZnO nanowires at low temperature [14]. An intermediate layer or a seed layer [15] is normally required in this technique. Recently, the ZnO seed layer has been adopted to assist the growth of ZnO nanowires and has been widely reported [16,17]. On the other hand, instead of using ZnO seed layer, noble metal thin films such as Ag and Au nano-particle films were deposited to grow ZnO nanowires. The noble metal nano-particle layer not only serves as bottom electrode but also enables the enhancement of the intensity of photoluminescence emission [18]. To understand the effects from the noble metal nano-particle layer on the as-grown nanowire structures and physical properties as well as, the nucleation mechanism of ZnO nanowire, gold nano-particle coated Si substrates were used to fabricate nanowires. Here, we report our recent studies on the effect of the gold nano-particle layer on the nucleation behavior of the ZnO nanowires synthesized with the hydrothermal technique.

2. Experimental

Si (111) wafers were chosen as substrates for fabricating ZnO nanowires. The gold nano-particle films with different thicknesses and controllable particle sizes were deposited on the as-selected substrates using magnetron sputtering. The gold nano-particle films were fabricated at room temperature using a Au (99.99% purity) target in Ar (99.999% purity) atmosphere with the pressure of 0.8 Pa and a power of 32 W. The thicknesses of the gold films were controlled by changing the sputtering time typically varying from 5 to 20 min. The gold coated Si wafers were then placed on the surface of aqueous solution, zinc nitrate,

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and hexamethylenetetramine, for 15 min at 75 °C. The samples were removed from the aqueous solution, cleaned with deionized water, and dried out in normal air. Surface morphologies of the gold nano-particle films were examined by atomic force microscopy (AFM, SPA-300HV, Seiko) before the ZnO nanowires were fabricated. The microstructures of the as-grown ZnO nanowires were characterized by the scanning electron microscopy (SEM, SSX-550, Shimadzu). The photoluminescence (PL) measurements were also conducted at room temperature on a spectrofluorophotometer (RF-5301, Shimadzu) using a Xe light excitation source with $\lambda = 325$ nm.

3. Results

Fig. 1(a)–(d) show the AFM images of the gold nano-particle films with the sputtering time varying from 5 to 20 min before the fabrication of ZnO nanowires, respectively. It is clearly seen that the particle size increases from 30 to 68 nm as the sputtering time increases from 5 to 20 min. ZnO nanowire arrays were fabricated on the gold coated Si substrates. Fig. 2(a)–(d) show the SEM images of the as-fabricated ZnO nanowires. The density of ZnO nanowires decreases as the particle size of the gold nano-particle films increases. On the other hand, the diameter and the length of the ZnO nanowires increase when the density of ZnO nanowires decreases. The size of nanowires is found to be highly dependent upon the nanowire nucleation density. Since the nanowires were synthesized in the same Zinc aqueous solution it is very likely that the higher density of the nucleation sites on the substrate the less Zinc in the aqueous solution for the single site. Therefore, the high density nucleation would lead to a smaller and shorter ZnO nanowire. Obviously, the particle size of the gold nano-particle films affects the ZnO nanowire density and the diameter as well as the length of ZnO nanowires. Usually, the grain size of gold thin films can be easily controlled by changing the deposition time of the gold thin film. The correlation between the density of ZnO nanowire and the particle size of the gold nano-particle films indicates that the density of ZnO nanowires can be controlled by changing the deposition time of the gold nano-particle films.

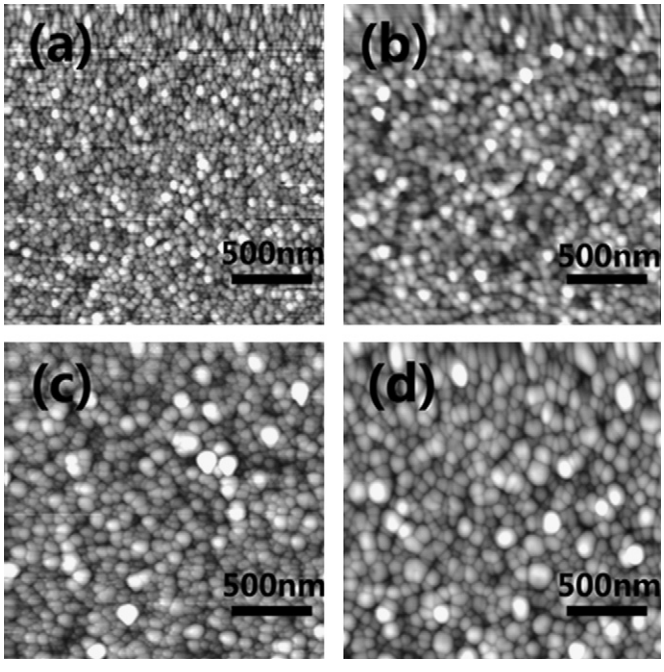

Fig. 1. AFM images of the gold nano-particle films grown on Si(111) substrates via sputtering for different times: (a) 5 min; (b)10 min; (c)15 min; and (d) 20 min.

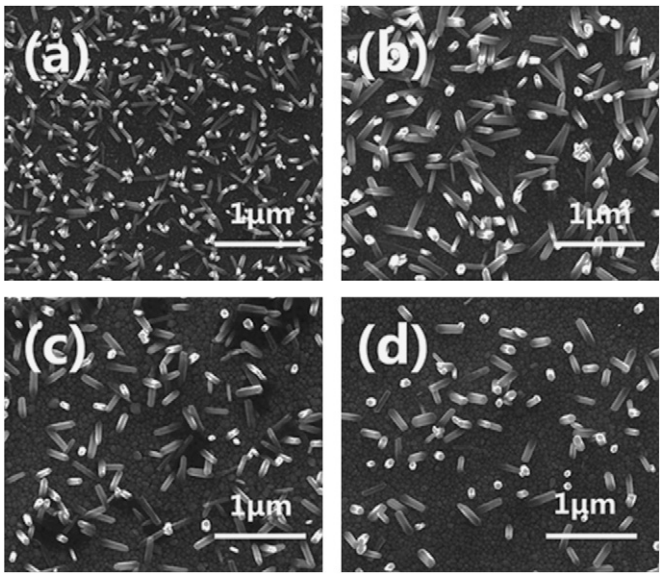

Fig. 2. SEM images of the ZnO nanowires grown on the gold coated Si substrates corresponding to Fig. 1.

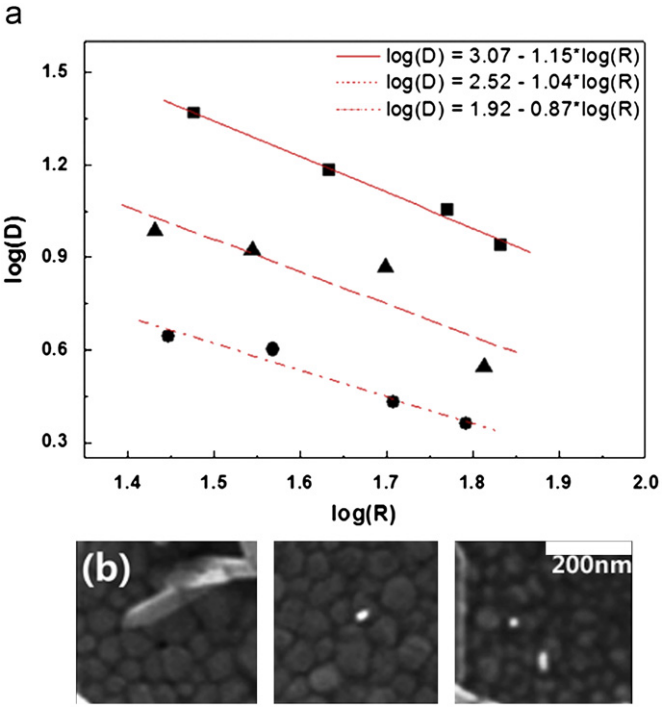

Fig. 3. (a) Log–log plot of the density of ZnO nanowires vs the particle size of the gold nano-particle films. (b) Enlarged SEM images of selected area in Fig. 2 showing some tiny ZnO nanowires could be found at the particle boundaries.

It is interesting to note that ZnO nanowires are likely nucleated at the grain boundaries of the gold nano-particle thin films. As seen in Fig. 3(b), all short ZnO nanowires were ended up at the gold nano-particle boundaries, implying that the ZnO nanowire may nucleate at the boundary. To understand the formation mechanisms of the ZnO nanowires, one assumes that the gold nano-particles are uniformly distributed with cubic grains (for simple analysis).The average size of the gold nano-particles, named as R, can be experimentally estimated from AFM images. The number of the gold nano-particles (N_{Au}) in the