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Initial Stages of GaAs/Au Eutectic Alloy Formation for the Growth of GaAs Nanowires

(Peringkat Awal Pembentukan Aloi Eutektik GaAs/Au bagi Pertumbuhan Nanowayar GaAs)

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ABSTRACT

Annealing temperature plays an important role in the formation of an Au-Ga eutectic alloy. The effects of the annealing temperature on gold nanoparticles colloid and substrate surface were studied using AFM, FE-SEM and TEM. At 600°C, the layer of gold colloids particle formed an island in the state of molten eutectic alloy and absorbed evaporated metal-organics to formed nanowire (NW) underneath the alloy. Pit formed on the substrate surface due to the chemical reactions during the annealing process have an impact on the direction of growth of the NW. Without annealing, the NW formed vertically on the GaAs (100) surface. The growth direction depends on the original nucleation facets and surface energy when annealed. When annealed, the wire base is large and curved due to the migration of Ga atoms on the substrate surface towards the tip of the wire and the line tension between the substrate surface and gold particle.

Keywords: Annealing process; GaAs nanowires; gold colloids

ABSTRAK

Suhu sepuhlindap memainkan peranan penting dalam pembentukan aloi eutektik Au-Ga. Kesan suhu sepuhlindap terhadap koloid nanozarah emas dan permukaan substrat dikaji menggunakan AFM, FE-SEM dan TEM. Dengan suhu 600°C, lapisan zarah koloid emas membentuk pulau-pulau yang berkeadaan aloi eutektik leburan dan boleh menyerap logam-logam organik terpeluap lalu membentuk nanowayar di bawah leburan tersebut. Liang yang terbentuk pada permukaan substrat akibat tindak balas kimia semasa proses sepuhlindap memberi impak pada arah pembentukan nanowayar. Tanpa di sepuhlindap, nanowayar yang terbentuk pada permukaan GaAs (100) adalah tegak lurus manakala arah pertumbuhan bergantung pada faset pernukleusan asal dan tenaga permukaan apabila disepuhlindap. Dengan sepuhlindapan, tapak wayar lebih lebar dan melengkung disebabkan penghijrahan atom Ga pada permukaan substrat menuju ke hujung dawai dan tegangan antara permukaan substrat dan zarah emas.

Kata kunci: Koloid emas; nanowayar GaAs; proses sepuh lindap

INTRODUCTION

GaAs is a III-V compound semiconductor material with a direct bandgap of 1.34 eV and a high electron mobility of 8500 cm^2/V.s. It has been widely used in electronic and optoelectronic devices such as field effect transistors (Lauhon et al. 2004), bipolar transistors (Wang et al. 2008), p-n juntions (Haraguchi et al. 1992) and NW lasers (Lieber 2003). GaAs NWs have been synthesized by a wide range of approaches such as metal-organic chemical vapour deposition (MOCVD) (Hiruma et al. 1995; Titova et al. 2006; Wacaser et al. 2006), molecular-beam epitaxy (MBE) (Ihn et al. 2007; Plante & LaPierre 2008), laser ablation (Xiangfeng et al. 2000), thermal evaporation (Wang et al. 2008) and chemical beam epitaxy (CBE) (Persson et al. 2004). By controlling the synthesis parameters, control has been demonstrated over the morphology, dimensionality and aspect ratio.

Metal catalyst particles are necessary in the formation of semiconductor NW via vapor-liquid solid method. This method was first discovered by Wagner and Ellis (1964). Because of the lattice mismatch between Au and semiconductor, the geometry and atomic structure of the interface have been found to be very critical to the NW growth. By regulation and preparation of the atomic structure of interfaces, it can help produce high quality NWs. Annealing temperature plays an important role in the eutectic alloy generated from Au nanoparticle catalyst and substrate surfaces. In the eutectic phase, Au nanoparticles can absorb vapours from the vaporization of the organic materials to form NW crystal underneath the droplet particle. Investigation of the annealing process has already been done by many researchers in the formation of GaAs NWs (Ghosh et al. 2009; Seifert et al. 2004; Wang et al. 2008). However, many studies and observations of colloidal gold particles on GaAs substrate at the early stages of formation was given less attention. Kawashima et al. (2008) studied the initial stages of Si NWs growth by transmission electron microscopy (TEM). Other groups reviewed on the initial formation of Au catalyst on the surface of the GaAs substrate using TEM and XRD (Ghosh et al. 2009; Mariager et al. 2010).

In this report, the formation of gold particles eutectic on the GaAs substrate at the early stages was investigated using atomic force microscopy (AFM). The AFM is ideally suited for both visualization of nanostructured materials and measuring the spatial dimensions of features at the surface of nanomaterials. Grain size, the shape of Au catalyst particles and pit residual before and after an annealing process can be differentiated. Field-Emission Scanning Electron Microscopy (FE-SEM) and Transmission Electron Microscopy (TEM) studies were also carried out for further investigation.

Experimental Works

The annealing process in this study was conducted in a vertical MOCVD reactor chamber at a pressure of ~76 torr. The experiment started with the substrates immersed in 0.1% poly-L-lysine (PLL) solution for three minutes, rinsed with de-ionized water and subsequently dried in nitrogen gas (N_2). The substrate used are GaAs (111)B and GaAs (100) wafer. B is a match for arsenic phase on top of the substrate. This purification process was done for three times. The 30 nm diameter gold colloid nanoparticles were then dispersed onto the substrate surface by using microlitre pipette and immediately washed with de-ionised water after 20 s. Due to the positively charged PLL layer, the negatively charged gold colloids are then attracted to it. The treated GaAs substrate was then, annealed in MOCVD reactor chamber at a temperature of 600°C for 10 min for agglomeration process. The V/III ratio, i.e. the total flow of arsine (AsH_3; 10% in H_2) over trimethylgallium (TMGa) was set at 166. The samples were then analyzed using an AFM, FE-SEM and TEM for structural and crystallographic characterization.

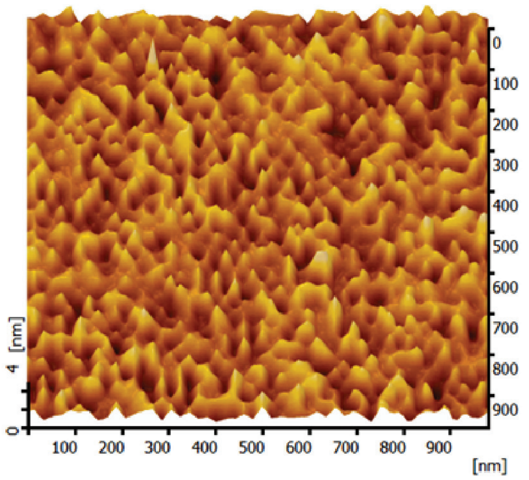
Results and Discussion

Effect of Annealing Temperature on Gold Colloid Nanoparticles and NWs

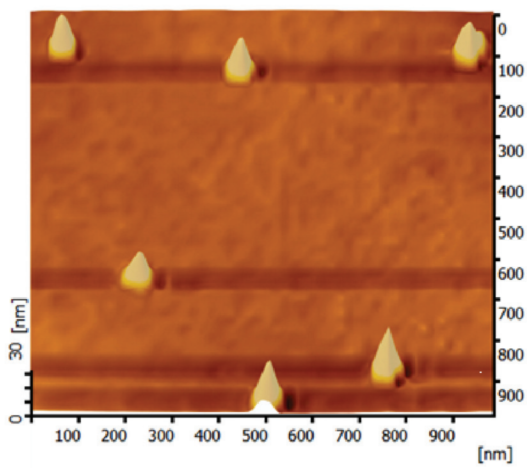
Figure 1 shows the AFM images captured before and after the annealing process of gold colloids layer under an arsine (AsH_3) ambient using a MOCVD reactor system. The substrate used was GaAs (111)B. Before the annealing process (Figure 1(a)), the roughness of the surface of gold colloids was 4 nm. From the enlarged areas in Figure 1(a), there are several particles overlapping each other. This surface layer contains oxide particles and impurities formed during the chemical and cleaning preparation. After thermal annealing process at 600°C for 10 min (Figure 1(b)), the layer of particle gold colloids agglomerates and form droplets with an average diameter of 50 nm. The average height of the droplets after annealing is 30 nm. From the magnified image, the droplet has a smooth shape of globule compared with the surface before annealing process with profile steps height and particles overlapped. The diameter of the base globule is about 80 nm as can be seen in the cross-sectional figure.

Figure 2 shows FE-SEM images of GaAs NW grown on GaAs(111)B substrate with and without annealing process. It is clearly shown that without annealing process, NWs grew randomly and broken. Meanwhile, with annealing, NWs grew perpendicularly to the substrate surface. For the NW growth process, the Au particles catalysts need to be ready in the molten state. If the state is solid (no annealing process or low annealing temperature), it could not absorb the Ga and As atoms from the TMGa and AsH_3 precursors. Therefore, it will not lead to NW growth or the growth direction would be scattered and easily broken.

The functions of metal particles are to absorb the atoms from vapour phase or substrate surfaces and to precipitate or crystallize the source materials at the particle-substrate

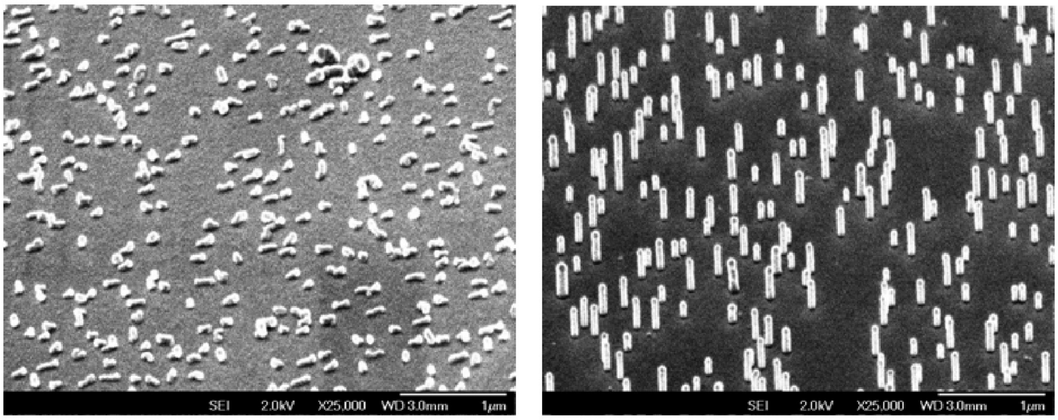


(a)



(b)

FIGURE 1. AFM images of particle gold colloids on GaAs (111)B substrate: (a) before annealing process and (b) after 600°C annealing process under AsH_3 ambient for 10 min



(a) (b)

FIGURE 2. FE-SEM images of GaAs nanowires grown on GaAs(111)B substrate. (a) Without annealing process on the gold colloids particle. (b) With annealing process at 600°C for 10 min

interface (Messing et al. 2009). The driving force of annealing temperature is to lower the chemical potentials of the source atoms. It has been observed that, the critical annealing temperature of the gold colloids for producing III-V nanowires was 540°C and above (Bhunia et al. 2004). For the GaAs nanowires, the annealing temperature of the gold colloids was 600°C when using the MOCVD due to perfectly alloying of the Au catalyst particles and GaAs substrate (Hannah et al. 2008; Hiruma et al. 2006). High activation temperatures (more than 700°C) may cause evaporation of the catalysts (Wang et al. 2008).

The nucleation and alloy between Au and GaAs surface produced Au-Ga eutectic point but not the Au-GaAs. This finding was reported by Tjong (2006) using an electron energy-loss spectroscopy and X-ray energy dispersive spectroscopy regarding the chemical composition of the catalysts after annealing process. The catalysts comprised of Au and Ga without As and O_2. The reaction of the catalyst and the surface is described as follows:

$$2\text{GaAs (solid)} + \text{Au (solid)} \rightarrow \text{AuGa}_2 \text{ (solid)} + 2\text{As (gas)}.$$

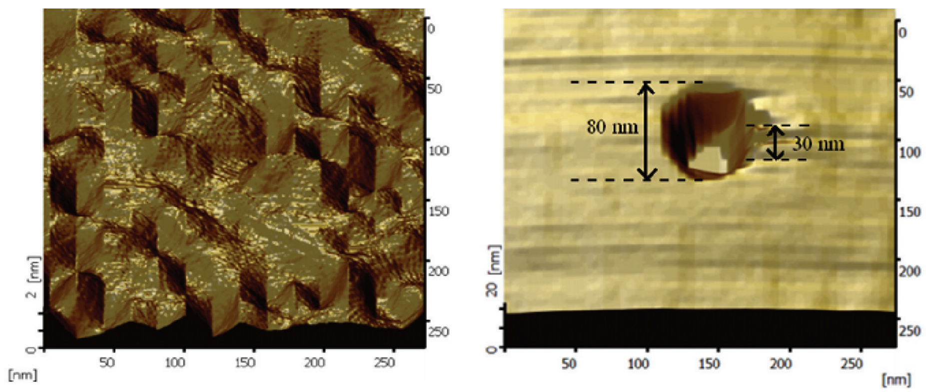
Referring to the above equation, arsenic is extracted from the substrate surface during the formation of $AuGa_2$ alloy. It may diffuse out of the catalyst surface and evaporates. The solubility of Ga depends on the size of catalysts due to the Gibbs-Thomson effect as reported by Huang and Kaner (2004). The smaller the catalyst size, the lower the temperature needed to melt the eutectic alloy and hence shifts the melting point of the catalyst as in Au-Ga phase diagram.

EFFECT OF ANNEALING TEMPERATURE ON SUBSTRATE SURFACE

A chemical reaction between gold particles and the substrate surface occurred during the annealing process. Figure 3 shows an AFM image of the resulting pit caused by the annealing process on the GaAs(100) substrate surface. The substrate was initially placed in an ultrasonic bath for 40 min to split the Au particles on the substrate surface. The Au particle were then detached from the surface and formed pit as shown in Figure 3(b) due to the 40 min sonication process in the acetone solution. The surface hole is 80 nm diameter and greater than the depth of the hole, 30 nm. It showed that the eroded surface of the substrate is much larger than the pit depth and easier to process compared with the digger. Similar observation was reported by Ghosh et al. (2009). They found that from TEM observations, various dimensions of size and orientations of the pits produced on the surface of GaAs(100), which depended on the orientation of Au particles on the surface of the substrate and the oxide. Figure 3(a) shows no obviously pits formed, except the rough surface. This was probably due to the attraction of gold colloids and substrate surface in the early process of substrate preparation.

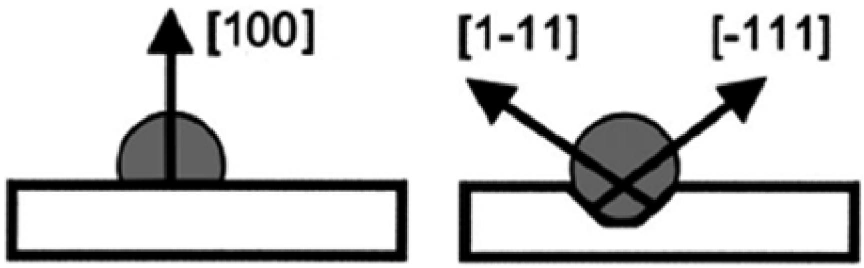
In the case of NW formation, the depression or hole in the substrate surface can affect the formation of NW. This phenomenon on can be explained using schematic diagram as shown in Figure 4. At a high temperature (600°C) GaAs substrate surface will be locally dissolved in the reaction with the Au as shown in Figure 4(b). Typical Au/semiconductor interfaces which develop under such conditions within the pit are the low-energy facets (111)B. These findings are related with report by Krishnamachari et al. (2004). They found that nucleation on such facets could be the starting point for the commonly observed whisker growth in [1-11] and [-111]. Annealing at lower temperatures (< 600°C) or in our case without annealing process, the GaAs(100) surface underneath the Au particle will not be attacked and when reaching a critical supersaturation due to supply of TMGa, nucleation for NW growth can start at intact Au/GaAs(100) interface. Consequently, NW growth may be prominent in the <100> direction.

Figure 5 shows TEM images of the GaAs NW. The close-up image is the base of the NW which is 5 times larger



(a) (b)

FIGURE 3. AFM image of GaAs (111)B substrate surface after annealing process on the gold colloids. (a) The surface roughness of the substrate is high without annealing process. (b) The hole occurred was due to the annealing process on the Au nanoparticle, meanwhile the surface of the substrate is smooth



(a) (b)

FIGURE 4. Schematics growth directions by start (nucleation) conditions; (a) growth from an Au droplet at the GaAs(100) surface after annealing and (b) growth from a Au droplet without annealing. Adapted from Krishnamachari et al. (2004)

from the original sizes. The bottom of the base is slightly curved and this suggests a chemical reaction between the NW and the substrate surface. The result is almost similar to that reported by Banerjee et al. (2006). They found that the root-like shape of GaAs NW base was caused by the chemical interaction at the early stage of the nucleation and growth via the VLS process. The interface layer between the roots and the substrate surface contained several lines of black and white stripes that are recognized as wurtzite and zincblende layers structure. These layers often arise in a semiconductor NW, especially at the base part, due to the propagation of Ga atoms on the substrate surface towards the NW tip at the nanoparticle Au (Rosnita et al. 2009; Hannah et al. 2007). The formation of this root structure at the NW/substrate interface is likely to influence the mechanical stability as well as the electrical transport properties of the NWs.

Figure 6 shows the FE-SEM images of GaAs (100) substrate after sonicated for 40 min. The process is for splitting NWs from the substrate surface and same for the process in the Figure 3(b). Some NWs were stuck to the substrate surface, but lying horizontally during the sonicating process. Close-up image of two circled particles are the root of NWs that grew intact to the surfaces (Circle 1). The dotted circle (2) was due to depression during the annealing process. The annealing process on the colloid particles was shown to lead to the formation of oriented pores in the GaAs single crystal surface. Bokhonov and Korchagin (2000) found that heating has a substantial impact on the character of the solid reaction products evolution. They also detects that a rapid propagation of the interface from gold particle on the surface into the semiconductor films occurred during heating by electron beam. The large NW base may also be due to the line tension. This phenomenon was reported by Wang et al. (2008). They observed that a large line tension can result in hillock growth of NW. The line tension is difficult to determine experimentally, however they have investigated using chemical-tension model and predicted that different line-tension values can result in NW or nanohillock growth.

CONCLUSION

Annealing temperature is an important parameter in the formation of Au-Ga eutectic alloy. The temperature of 600^{o}C was able to produce molten state between the nanoparticle Au and Ga atoms and absorbs metal-organics

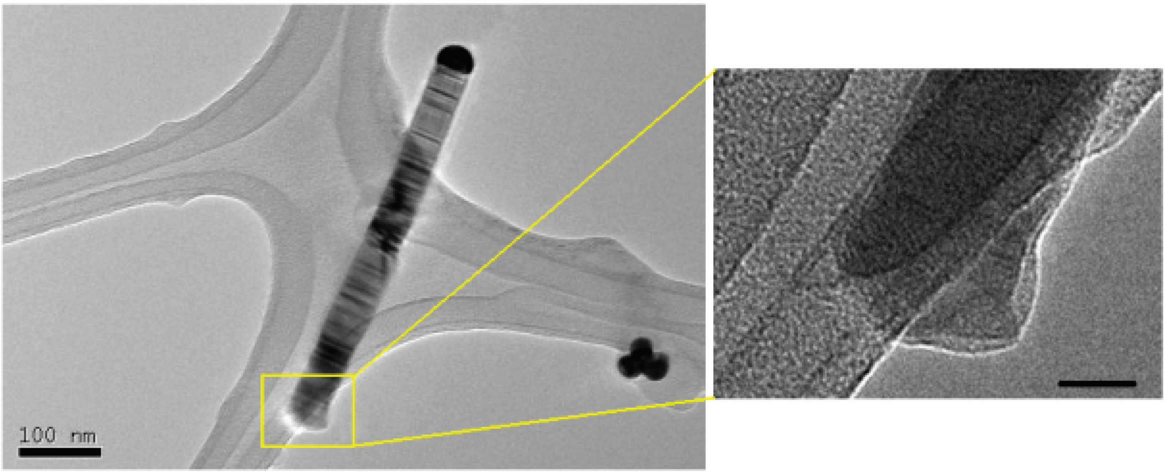
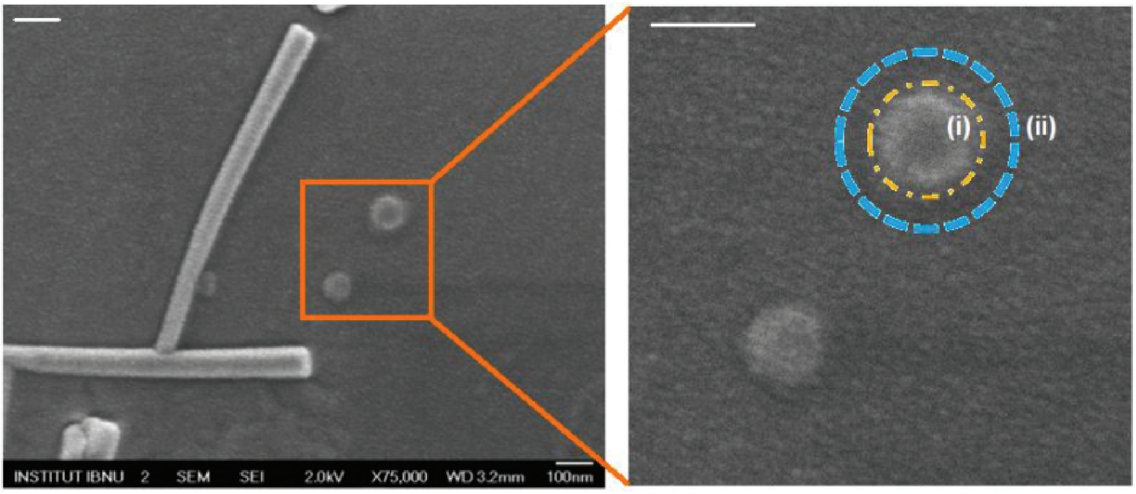


FIGURE 5. TEM images of GaAs nanowire. The 5X magnified image of the base of nanowire shows curved shape that was due to chemical reaction during the annealing process. The scale bar in magnified image is 20 nm



(a) (b)

FIGURE 6. (a) FE-SEM images of GaAs(111)B base residual with notch shape. (b) Magnified image of base residual. The notch shaped was caused by annealing processes on the nanoparticle gold colloids. The scale bar in both image are 100 nm

for growing NW crystal. Besides the benefit of annealing process, it also resulted in the substrate surface damaging by producing pit between alloy and substrate surface. Therefore, the NW will grow intact at the facet with lower energy and caused more stripes with defect structure. The initial stages of the Au-GaAs eutectic alloy have been succesful investigated by AFM, FE-SEM and TEM equipments.

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