The Effect of Annealing Temperature on Gold Catalyst and Substrate Surface in the Growth of GaAs Nanowire

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ABSTRACT

Annealing temperature plays an important role in the formation of Au-Ga alloy eutectic. Effect of annealing temperature on gold catalyst and substrate surface were studied using AFM, FE-SEM and TEM. With a temperature of 600 °C, the layer of gold colloids particle formed an islands in the state of molten eutectic alloy and absorbed evaporated metal-organics to formed nanowire underneath the alloy. Pit formed on the substrate surface due to the chemical reactions during the pre-annealing process have an impact on the direction of nanowire growth. Without pre-annealing temperature, the nanowire formed vertically on the GaAs (100) surface, meanwhile the growth direction depends on the intact nucleation facets and surface energy, when annealing is applied. With pre-annealing temperature, the wire base is large and curve due to the migration of Ga atoms on the substrate surface towards the tip of the wire and line tension between the substrate surface and gold particle.

1. INTRODUCTION

Metal catalyst particle are necessary in the formation of semiconductor nanowire via Vapor-Liquid Solid method. This method was first discovered by Wagner and Ellis (Wagner & Ellis, 1964). Because of the different lattice between Au and semiconductor, the geometry and atomic structure of the interface have been found to be very critical to the nanowire growth. By regulation and preparation of the atomic structure of interfaces, it can help produce high quality nanowires. 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 nanowire crystal underneath the droplet particle. Investigation of the annealing process has already been done by many researchers in the formation of GaAs nanowires (Seifert, et al., 2004, Ghosh, et al., 2009 & Rosnita, et al., 2012). 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) have reported the initial stages of Si nanowires growth using 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 performed using atomic force microscopy (AFM). The AFM is ideally suited for both visualization of nanostructured materials and for 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 TEM were also carried out for further investigation.

2. EXPERIMENTAL WORKS

Annealing process in this study was conducted in the vertical MOCVD reactor chamber at a pressure of ~76 Torr. The experiment started with the GaAs(111)B and (100) 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). This purification process was done for two or three times. The nanoparticle gold colloids were then dispersed onto the substrate surface by using microlittre pipette and immediately washed with de-ionised water after 20 seconds. The diameter of the gold colloids used are 30 nm. Due to the positively charged PLL layer, the negatively charged gold colloids are then attracted to it. The treated GaAs substrate was annealed in MOCVD reactor chamber at a temperature of 600 °C for 10 minutes. For the growth of GaAs nanowires, Trimethylgallium (TMGa) and arsine (AsH_3; 10% in H_2) were used as gas sources and V/III ratio was set at 166. The samples were then analyzed using an AFM, FE-SEM and TEM.

3. RESULTS AND DISCUSSIONS

3.1 Effect of annealing temperature on nanoparticle gold colloids.

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 unsmooth surface layer of gold colloids with roughness of 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 during the chemical and cleaning preparation. After thermal annealing process at 600 ^{o}C for 10 minutes (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 is 30 nm. From the magnified image, the droplet has a smooth shape of globule compared to the surface before annealing process with profile steps height and particles overlapped.

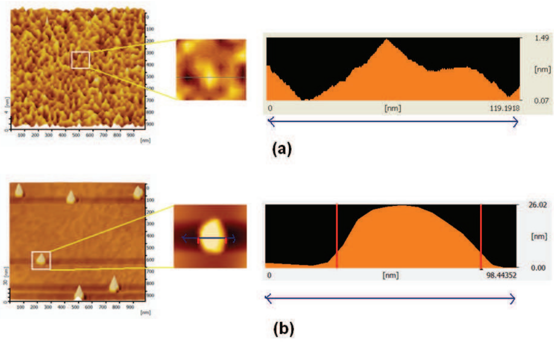

Fig. 1. AFM images of particle gold colloids on GaAs (111)B substrate : (a) before annealing, (b) after 600^{o}C annealing process under AsH_3 ambient for 10 min.

The nanowire formed underneath the droplet when the Au particles catalysts are in the molten state. If the state is solid, it could not absorb the Ga and As atoms from the TMGa and AsH_3 precursors. Therefore, it will not lead to vertical nanowire growth and the growth direction would be scattered and also easily broken as shown in Figure 2. The function of the metal particles are : (1) to absorb the atoms from vapour phase or substrate surfaces and (2) to precipitate or crystallize the source materials at the particle-substrate interface (Messing, et al., 2009). It has been observed that, the critical annealing temperature of the gold colloids for producing III-V nanowires was 540 ^{o}C and above (Bhunia, et al., 2004). For the GaAs nanowires, the annealing temperature of the gold colloids was 600 ^{o}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 may cause evaporation of the catalysts.

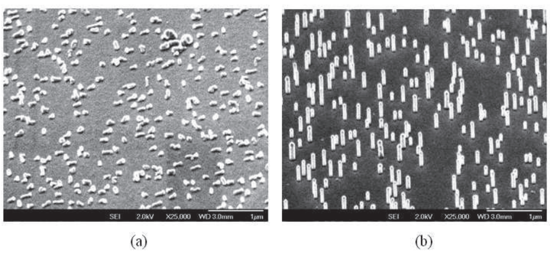

Fig. 2. FE-SEM images of GaAs nanowires grown on GaAs(111)B substrate. (a) Without annealing process on the gold colloids particle. (b) With annealing process at 600 ^{o}C for 10 minutes.

The nucleation and alloy between Au and GaAs surface has produced Au-Ga eutectic point but not the Au-GaAs. This findings 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 detectable of As and O_2. The reaction of the catalyst and the surface is described as follows,

$$2GaAs\ (solid) + Au\ (solid) \rightarrow AuGa_2\ (solid) + 2As\ (gas)$$

Referring to the above equation, arsenic is extracted from the substrate surface during the formation of $AuGa_2$ alloy. It may diffuse out of 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.

3.2 Effect of annealing temperature on GaAs 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 the ultrasonic Branson to split the Au particles on the substrate surface. The Au particle when detached from the surface formed hole due to the process of chemical reaction as shown in Figure 3(b). The diameter of the surface hole was greater than the deep hole. It showed that the eroded surface of the substrate is much larger than the one inside. Similar observation was reported by Ghosh (2009). From the TEM observation, they found that various dimensions of size and orientations of the pit produced on the surface of GaAs(100) which depended on the orientation of Au particle on the surface of the substrate and the oxide. As for reference, Figure 3(a) shown no obviously pit formed, except the roughness surface. This was probably due to the attracted process of gold colloids and substrate surface in the early process of substrate preparation.

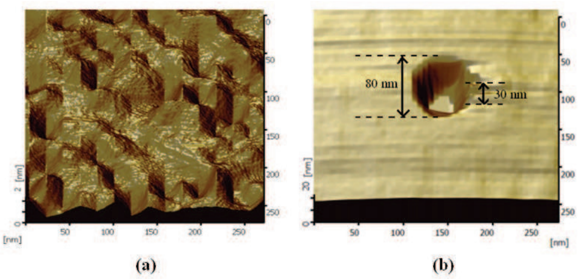

Fig. 3. AFM image of GaAs (111)B substrate surface after annealing process. (a) The surface roughness is more prominent without annealing process. (b) The hole

occurred was due to the annealing process on the Au nanoparticle.

In the case of nanowire formation, the depression or hole in the substrate surface can affect the formation of nanowire. This phenomena can be explained using schematic diagram as shown in Figure 4. At a high temperature (600^{o}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 (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 ^{o}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 nanowire growth can start at intact Au/GaAs(100) interface. Consequently, nanowire growth may be prominent in the <100> direction.

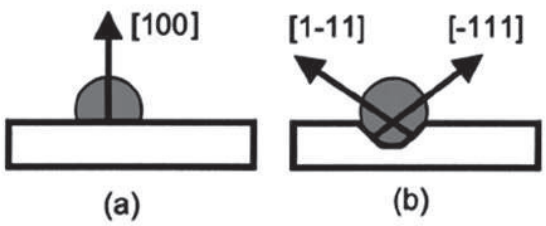

Fig 4. Schematics growth directions by start (nucleation) conditions; (a) growth from an Au droplet at the GaAs(100) surface after annealing and (b) growth from a Au droplet without annealing. Adapted from Krishnamachari, et al. (2004).

Figure 5 shows TEM images of the GaAs nanowire. A close-up image (5X original image) is the base of the nanowire. The bottom of the base is slightly curved shape and this suggests a chemical reaction between the nanowire and the substrate surface.

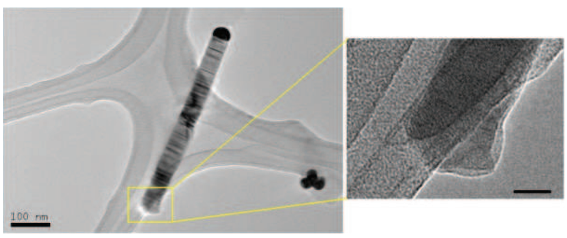

Fig. 5. TEM images of GaAs nanowire. The 5X magnified image of the base of nanowire shows curved shape that was due to chemical reaction during the annealing process. The scale bar is 20 nm.

The result is almost similar to that reported by Banerjee, et al. (2006). They found that the root-like shape of GaAs nanowire 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 nanowire, especially at the base part, due to the propagation of Ga atoms on the substrate surface towards the nanowire tip at the nanoparticle Au (Rosnita, et al., 2009 & Hannah, et al., 2007). The formation of this root structure at the nanowire/substrate interface is likely to influence the mechanical stability as well as the electrical transport properties of the nanowires.

Bokhonov and Korchagin (2000) found that heating method 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 amorphous silicon film was occurred during heating by electron beam supply. The large of base nanowire may also 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 nanowire. The line tension is difficult to determine experimentally, however they have been investigated using chemical-tension model, and predicted that different line-tension values can result in nanowire or nanohillock growth.

Figure 6 shows GaAs substrate after sonicated in an acetone solution. The process is for splitting nanowires from the substrate surface. There are some nanowires that are still attached to the substrate surface but lying horizontally during the sonicating process. Close-up image of two circled particles are the balance of splitting nanowires which are broken. The dotted circle (ii) was due to depression during the annealing process and rounded the broken remaining nanowire (i).

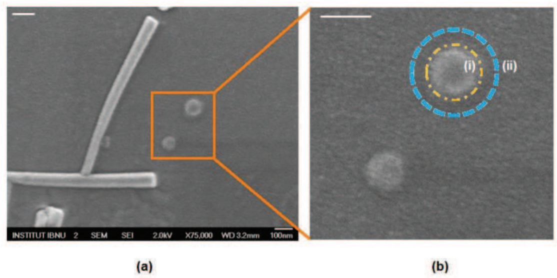

Fig. 6. (a) FE-SEM images of GaAs(111)B base residual with notch shape, (b) Magnified image of base residual. The notch shaped was caused by annealing processes on the nanoparticle gold colloids. The scale bar in both image are 100 nm.

CONCLUSION

Annealing temperature is an important process in the formation of Au-Ga alloy eutectic. The temperature of 600 ^{o}C was able to produce molten state between the nanoparticle Au and Ga atoms. It also can lead to vertical nanowire growth on the GaAs(111)B substrate. Selection of a suitable annealing temperature can prevent chemical reactions between the particle and the semiconductor surface. With AFM, nucleation of nanoparticle gold colloids and the formation of pit due to the chemical reactions can be clearly observed and obtained. FE-SEM and TEM studies support the results.

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