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SOME RESULTS OF THE NANOWIRES GROWTH ON GALIUM ARSENIC SUBSTRATE BY VLS METHOD: SOME THEORETICAL ASPECTS OF THE GROWTH MECHANISMS AND ABNORMAL PHENOMENA

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Abstract. *This paper reports some main theoretical and practical aspects of Vapor-Liquid-Solid (VLS) mechanism on GaAs substrate. And the paper also briefly outline some new phenomena: the Au droplets/clusters formation as well as the nanowire growth phenomena in the region without Au that are as the results of the out diffusion of Au outward to the region up to 40 or 80 μ from an Au layer edge depending on growth temperature; the etching process so called the reverse VLS, and the formation of the empty Au voids in an thicker Au layer during the nanowires growth process. Some our experimental results of synthesis of GaAs semiconductor nanowires are briefly shown and discussed.*

I. INTRODUCTION

The nanowires (NWs) have many interesting properties such as: the dimensions are controllable, tunable conductivity, variable band gap, flexible surface chemistry, increased surface area, enhanced exciton binding energy, diameter-dependent bandgap, increased surface scattering for electrons and phonons, that they can be used in nanoscale opto-electronic devices (LASER, LED, and Sensors). The nanowires have been growing by different method .... Among synthesis methods, the VLS method is a simple, popular, cheap method [1, 2]. However, the structural, electrical, optical properties as well as the morphology of nanowire grown by the VLS method strongly depend on many factors such as the growing temperature, Au thickness layer, vapor pressure, the diffusion process of Au catalyst metal, the size effect and physical properties of the liquid alloy ...) which are not yet clearly understood [2, 3]. In this paper, continuing several previously works [8], we outline some theoretical and practical aspects, especially the effects of Au catalyst metal with 200 nm thickness, the diffusion -formation of Au droplets/clusters outward and the nanowire growth process inside and outside of Au layer in the wide range of technological conditions.

II. SOME PROBLEMS CONCERNING NANOWIRES GROWTH

II.1. VLS growth method

The VLS is a mechanism for the growth of nanowires, nanorods, nanotubes. The VLS mechanism was proposed in 1964 as an explanation for silicon whisker growth [4] then

this method has been developing for growing the nanowires on GaAs substrate [5, 6, 7]. The VLS mechanism consists of introducing a catalytic liquid alloy phase which can rapidly adsorb a vapor to supersaturation levels, and from which crystal growth can subsequently occur from nucleated seeds at the liquid-solid interface [7, 8].

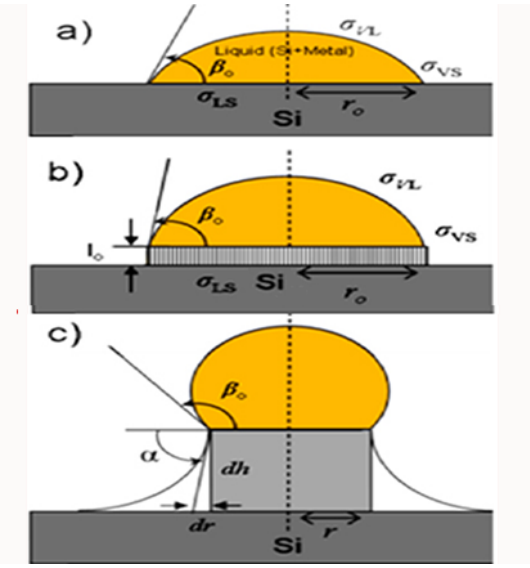

Fig. 1. The droplet variations together with variations of the β_0 contact angle together with tensions components in Si substrate where σ_{SV} is the solid -vapor surface tension, σ_{LS} is the liquid-solid interface tensions and σ_{LV} is the liquid -vapor surface tension. a,b) and the inclination angle (α) is formed at the flank of the nanowire during growth nanowire c) [7]. The same situation could be modeled for GaAs substrate

II.2. The shape of the Au droplet

The shape of the Au droplet is crucial for nanowire growth by VLS method. The shape of a catalyst particle at the surface of a crystalline substrate is determined by a balance of the forces of σ_{VL} surface tension and the liquid-solid interface tension (σ_{LS}). The radius of the droplet varies with the contact angle (β_0) as [5, 6, 7]:

$$R = \frac{r_0}{sin(\beta_0)} \tag{1}$$

where r_0 is the radius of the contact area on the solid surface and β_0 is the contact angle (fig. 1. As a nanowire begins to grow, its height increases by an amount dh and the radius of the contact area decreases by an amount dr, then the nanowire growth continues, the inclination angle (α) at the base of the nanowires increases from the zero value, in this case the Young's equation is modified some what that equation can be rewritten in the following form [5, 6, 7]

$$\sigma_{LV}.cos\beta_0 = \sigma_{SV}cos(\alpha) - \sigma_{SL} - \frac{\tau}{\tau_0} \tag{2}$$

where σ_{SV} is the solid -vapor surface tension, σ_{LS} is the liquid-solid interface tensions and σ_{LV} is the liquid -vapor surface tension. The third term in the right hand of the (2) equation comes from the effect when the initial radius of the droplet is nanosized which has an additional line tension (τ). The term of the line tension (τ/r_0) greatly influences the catalyst contact area and one will result in different growth modes with different line tensions.

II.3. The main driving force

The main driving force $\Delta\mu$ for nanowire growth in the supersaturation of the metal droplet can be written as the following [5, 6, 7]

$$\Delta\mu = \Delta\mu_0 - \frac{4\gamma_0\Omega}{d} \tag{3}$$

where $\Delta\mu_0$ is the difference between the chemical potential of the depositing species in the vapor phase and solid whisker phase. $\Delta\mu$ is the initial difference proceeding whisker growth (when d$\sim \infty$), d is diameter of nanowire, Ω is the atomic volume of substrate material concerning and γ_0 is the specific free energy of the wire surface.

II.4. The different morphologies of NWs

The different morphologies of NWs are often appeared during the nanowire growth that due to the effects of monocentric and polycentric nucleation and its combination with periodic stable and unstable growth. The morphologies of NWs could be: i) the uniform diameter of the trunk and branches in polyp-shaped nanowires; ii) the amoeba-shaped nanowires are a result of monocentric nucleation; iii) the frog-egg shaped nanowires. Some problems are still not clearly, the nanowire can growth easily in supersaturation levels, but in an equilibrium situation or bellow equilibrium the nanowires could be grown by VLS mechanism or not? We could not understand more clearly about these cases. One has also offered the minimum radius of a metal droplet in an equilibrium situation that is given by [5, 6, 7]

$$R_{min} = \frac{2V_L}{RTln(s)}\gamma_{LV} \tag{4}$$

where V_L is the molar volume of the droplet, γ_{LV} the liquid-vapor surface energy, and s is the degree of supersaturation of the vapor. This equation restricts the minimum diameter of the droplet. There are still also some argumentations about the growth mechanisms in VLS method. One could often consider the presence of the nearly spherical nanoparticles lying-staying on the tops of the nanowires to be a strong evidence of the vapor-liquid-solid (VLS) growth mechanism. Several works [2, 3, 7] stated that other growth mechanisms, such as the vapor - solid - solid mechanism, could be dominated during the nanowire growth by VLS method on the III-V semiconductor substrate.

III. EXPERIMENTAL PROCEDURES AND THE RESULTS

III.1. The experiments

The experiments in this paper are similar to previous our work [8]. Here there are several points that are different: Starting materials used in our experiments were the n-type GaAs slices with (100) orientation. A thin catalyst layer of Au were sputtered

onto the front side surface of GaAs , their thicknesses are approximately 200 nm and 1000 nm. GaAs slices were treated chemically and the samples were heated in three zone vacuum furnaces by VLS method with two temperature mode. The temperature profile for nanowire growth can see in Fig. 2b The samples were investigated by a FESEM on FESEM-Hitachi S-4800 equipment, energy-dispersive X-ray (EDX) techniques, AFM equipment

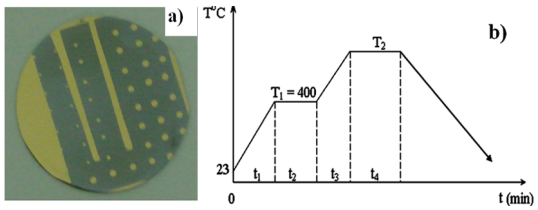

Fig. 2. a,b) Photographs of GaAs slice with Au sputtered circle, strips configurations for experiments a), and the nanowire growth by two steps temperature profile mode b)

III.2. The new experimental results -abnormal phenomena

III.2.1. *The Au diffused outward*

The Au droplets/clusters formed outside far from Au stripe edge up to 40 μm and the nanowires growth there in the absence of Au layer We can see on the Fig. 3 that NWs

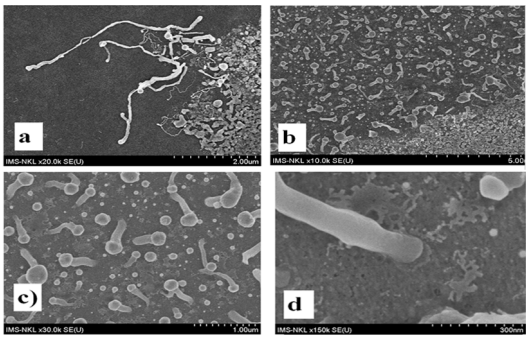

Fig. 3. FESEM micrographs at the edge of M5 V200 sample with 200nm thickness sputtered Au stripe. The growth conditions at $T_1 = 410^oC$ in time $t_2 = 20$ min, and $T_2 = 620^oC$ in time t_4=30 min), pressure is about 10^{-1} torr. Au out diffused a), and NWs grown far from Au layer edge b,c,d)

did not grow inside Au stripe in this case (see on Fig. 3a,b), meanwhile the Au had diffused far from Au layer edge and the droplets/clusters formed with decreasing diameters, the nanowires have also grown on the region absence Au on substrate. the size of NWs are about 40-60 nm with coarsen diameters. The same phenomena have been observed for the other samples.The structures of NWs in these cases are also having been investigated by EDX and the NWs have the almost same contains: 34.17% O, 51.94% Ga and 13.89% As [10, 11].

III.2.2. *The Au empty Voids configurations formed inside the Au layer*

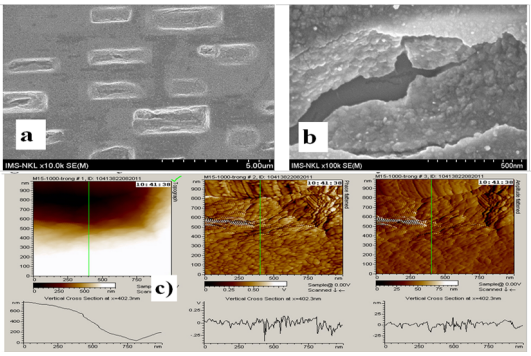

Fig. 4. FESEM micrographs on M15 T200 sample with 200nm Au thickness: Au empty voids formed a,b) and AFM micrographs of a Au empty void showing void deep image (it is about 700 nm) , phase image and amplitue image in comparision with the base level). The growth conditions: T_1= 440^oC in t_2 = 20 min and T_2 = 610^oC in t_4=30 min.

So far the reason of the voids formation have not been reported and explained clearly for the nanowire growth process, but the similarly phenomenon was reported during making the Au contact on GaAs semiconductor [10, 11], here the Authors have also stated that the low-temperature formation of voids in the gold lattice and crystallite growth on the gold surface, which are hard-to explain observations. We think that this phenomenon is related closely with the mechanism of dissolution of as and Gad into Au layer. We could explain that during Nano wire growth with a thicker Au layer (for our case), the equal amounts of Gad and As are entered into the gold lattice, then Arsenic evaporated from the free surface, since arsenic is insoluble in gold, meanwhile Gallium atoms enter the gold lattice and remains there. The evaporation of As, as well as the presence of Oxygen could be a reason for empty Voids formation.

III.2.3. *The etching phenomenon or Reverse VLS(Fig. 5)*

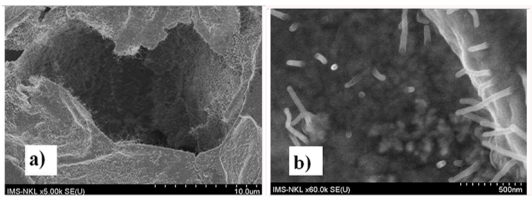

Fig. 5. a) FESEM micrographs of M6 V200 sample with 200nm Au thickness, the growth conditions at T_1 = 440^oC in t_2=20min and T_2 = 640^oC in t_4=30 min, the Au circle the etching hole a, b)

IV. CONCLUSION

We have successfully synthesized nanowires on the GaAs substrate using a thermal VLS method with two temperatures (T_1 and T_2) mode. We have observed three new phenomena: i) Au outdiffused from Au layer edge and the droplets/clusters formed together with nanowire growth; ii) the empty voids formation in Au layer and iii) etching substrate during nanowire growth. Inside the thick Au circles or strips layer, the NWs almost did not grow or hardly grow in very small diameter with no Au droplet on the top. Meanwhile the NWs have grown strongly in the results of Au diffusion and droplets/clusters formations in the outside of Au layer with coarsen diameter with the big Au droplets on the tops. The more further the Au layer edge, the smaller diameters of Au droplets/clusters, of course the smaller the nanowire diameters.

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