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Catalyst and its diameter dependent growth kinetics of CVD grown GaN nanowires

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ABSTRACT

GaN nanowires were grown using chemical vapor deposition with controlled aspect ratio. The catalyst and catalyst-diameter dependent growth kinetics is investigated in detail. We first discuss gold catalyst diameter dependent growth kinetics and subsequently compare with nickel and palladium catalyst. For different diameters of gold catalyst there was hardly any variation in the length of the nanowires but for other catalysts with different diameter a strong length variation of the nanowires was observed. We calculated the critical diameter dependence on adatoms pressure inside the reactor and inside the catalytic particle. This gives an increasing trend in critical diameter as per the order gold, nickel and palladium for the current set of experimental conditions. Based on the critical diameter, with gold and nickel catalyst the nanowire growth was understood to be governed by limited surface diffusion of adatoms and by Gibbs–Thomson effect for the palladium catalyst.

1. Introduction

Miniaturization of devices based on nanotechnology has led to increased interest in different nano-scale materials. Inorganic nano-structures exhibit peculiar and unique properties different from their bulk counterparts due to quantum effects and also due to large surface to volume ratio. In electronic, photonic and energy related applications GaN has become an important material for its superior properties in comparison to other semiconductors [1,2]. Most vital properties are its large bandgap, high melting point, carrier mobility, and electrical breakdown field. Additionally GaN exhibit spontaneous polarization and piezoelectric fields depending on growth orientations [3]. Such properties at the nano-scale would be of immense help in fabricating nano-devices using quantum dots and wires [4,5]. Though superior quantum effects are observed for quantum dots, nanowires have drawn more attention in the last decade. It is because of the difficulty in making contacts with quantum dots whereas, it is easy to make contacts with nanowires. However, diameter and aspect ratio control of nanowires has been challenging and important for the fabrication of nanowire based electrical and optical devices [6,7]. For catalysis growth of nanowires, the diameter of catalytic particle determines the diameter of nanowires. On the other hand length growth rate of nanowires depends on the diameter [8,9]. There have been theoretical models explaining the growth kinetics of nanowires grown by molecular beam epitaxy and metal organic chemical vapor deposition. However, extending these models for the analysis of nanowire grown by thermal chemical vapor deposition (CVD) has not been attempted. But it is very important to understand the growth kinetics for CVD grown nanowires. Johansson et al. proposed a mass-transport-limited diffusion model for calculating the diameter dependent length growth rate of nanowires [10],

$$\frac{dL}{dt} = \frac{2\Omega R_w \lambda_w}{r_w} \tanh\left(\frac{L}{\lambda_w}\right) - \frac{2\Omega J_{sw}}{r_w Cosh(L/\lambda_w)} + 2\Omega R_{top} \quad (1)$$

where L is the length of nanowire; t is the time; Ω is the the atomic volume of adatom in the catalyst particle; R_w is the deposition rate; λ_w is the diffusion length along the side of the nanowire; r_w is the radius of the growing nanowire; J_{sw} is the adatom flux and R_{top} is the nanowire radius at the tip.

In Eq. (1), the first term represented the diffusion of material directly deposited on the nanowire sidewalls, and the second term accounts for adatom diffusion from the substrate surface up along the nanowire. The third term accounts for the material deposited directly on the catalytic particle. This equation indicates that as the nanowire diameter increases the length decreases. However for very small but increasing diameters of nanowires, increase in nanowire length has also been reported [11,12]. Through a detailed modeling by taking into account both increasing and decreasing of length growth rate with increasing diameter was reported by Fröberg et al. [11]. Assuming that the direct impingement into

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catalytic particle is negligible, there seems to be a critical diameter below which length growth rate decreases with decreasing diameter due to Gibbs–Thompson effect (GTE) and above which length growth rate decrease with increasing diameter due to limited adatoms diffusion. The critical diameter is given by [11],

$$d_c = \frac{4\sigma\Omega}{kT\ln(P/P_\infty)} \tag{2}$$

where σ is the surface energy of the catalyst in its bulk form (J/m^2); Ω is the the atomic volume of adatom in the catalyst particle (m^3); k is the Boltzman's constant (J/K); T is the growth temperature (K); P is the adatoms vapor pressure in reactor (Pascal) and P_∞ is the adatoms vapor pressure inside the large (infinite radius) catalyst (Pascal). So critical diameter at which the nanowire attains maximum length is used to explain the growth kinetics. However, observable critical diameter depends chiefly on the ratio of adatoms pressure in the reactor to the adatoms pressure inside the catalyst. By controlling the catalyst particle diameter one can also control aspect ratio of nanowires. GaN nanowires with different catalytic particles have been reported by several groups [13–15]. But there are hardly any reports on controlling the nanowire diameter hence the aspect ratio by choosing proper catalyst and with suitable diameters. In addition to the catalytic particle, the growth condition is also very important to choose the growth kinetics. In this paper we demonstrate experimentally the control of growth kinetics by a suitable choice of catalyst, their diameters and growth conditions. We show that the mass transport limited diffusion model can explain the growth kinetics where the diffusion through nanowire sidewall dominates. Adoption of a suitable catalyst, its diameter with known growth kinetics is important to have controlled growth of nanowires for nano-scale device applications.

2. Experimental

2.1. Synthesis

GaN nanowires were grown on silicon substrates with thermally evaporated gold, nickel and palladium as catalysis with average particle diameters 120, 45 and 20 nm, respectively. For gold catalyst the average particle diameter was also varied to be 120, 85 and 50 nm. High purity gallium-metal and ammonia gas were used as source and the growth temperature and ammonia flow rates were fixed to be 1173 K and 25 standard cubic centimeter per minute (sccm), respectively. For all the cases the growth time was also fixed to be 3 h and the distance between the gallium source and growth substrate was about 3 mm [6].

2.2. Characterizations

The nanowires were characterized by field emission scanning electron microscopy (FESEM) (operated at 10 keV), transmission electron microscopy (TEM) (operated at 200 keV), energy dispersive analysis of X-rays (EDAX) and Raman spectroscopy. The Raman spectra were recorded using 514.5 nm of Ar-ion laser in the backscattering mode at room temperature. The laser power was 10 mW through a 20×-objective and the collection time was 10 s.

3. Results and discussion

Fig. 1(a)–(c) shows the SEM images of GaN nanowires varying gold catalyst particle diameters as, 50, 85 and 120 nm, respectively. The average nanowire diameters are 52, 85 and 115 nm which is close to the catalyst particle diameters. However, the striking feature is the same length (~3 μm) of the nanowires irrespective of their diameters and the reason for the same is discussed later. Fig. 2(a)–(c) shows the SEM images of GaN nanowires with Au, Ni and Pd catalyst and Fig. 2(d) is a high magnification image of Fig. 2(c). A clear aspect ratio variation is observed for different catalytic particles. For palladium catalyst only nanowires (and not other nanostructures) are analyzed and included for further discussions. In Fig. 2, the diameter of the catalyst particles were 120, 45 and 20 nm for gold, nickel and palladium, respectively and the nanowire diameters are almost equal to the respective catalyst particle sizes. The corresponding lengths measured for nanowires (almost horizontal to the substrate) are approximately 3, 7 and 1 μm, respectively. The composition of the nanowires were analyzed using EDAX measurements and were found to be almost 1:1 (of Ga:N) for gold catalyst but for nickel and palladium it was relatively nitrogen rich (please see Fig. S1 of the Supporting document for details). Figs. 1 and 2 are the experimental demonstration of aspect ratio controlled growth of GaN nanowires with suitable choice of catalysts. The diameter control is possible by varying the catalyst particle diameter. The average diameter reported here ranges between 20 nm and 120 nm with aspect ratio

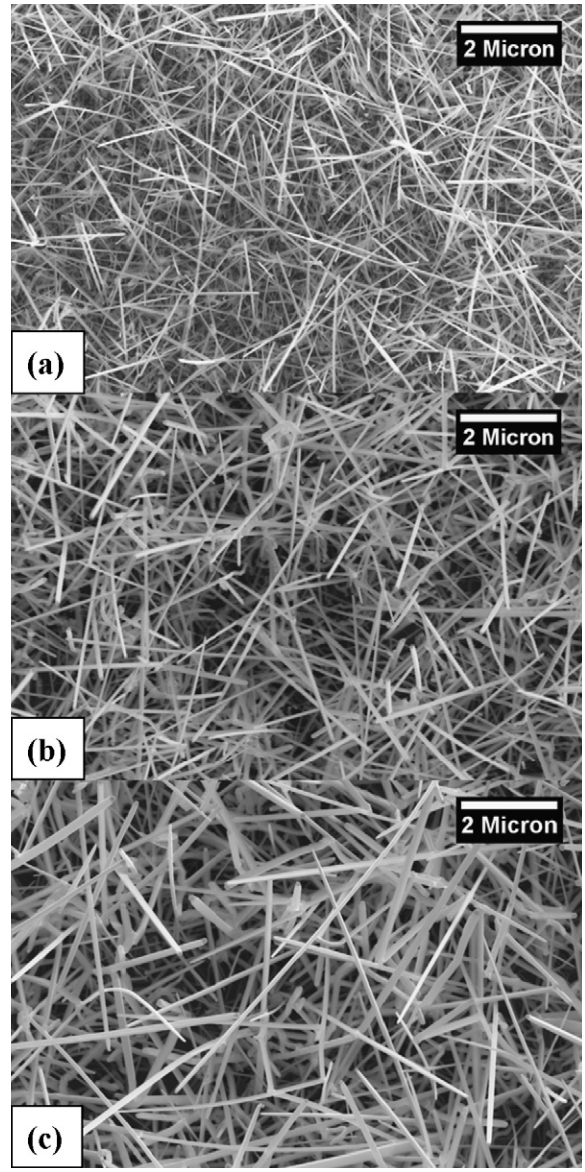

Fig. 1. SEM images of nanowires grown using gold catalyst with varying diameter (a) 50 nm, (b) 85 nm, and (c) 120 nm.