Brief communication

The structural and optical properties of gallium arsenic nanoparticles

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Abstract

Spherical gallium arsenic nanoparticles prepared by thermal evaporation method have been fabricated successfully. The structural and optical properties of GaAs nanoparticles are studied in detail. It is found that while the growth pressure rises from 0.4 to 5 Torr, the average size of GaAs nanoparticles increases from 6 to 12 nm and standard deviation keeps almost the same (~ 2 nm) except for 0.5 Torr. By using transmission electron microscopy and Raman spectra, a critical preparation condition has been found which characterize the amorphous to crystal transition of GaAs nanoparticles.

Introduction

Semiconductor hetero-structures with embedded quantum dots (QDs) having almost atomic-like energy levels have experimentally exhibited properties expected for zero-dimensional systems (Ekimov et al., 1985; Bryllert et al., 2002; Marsal et al., 2002; Yoffe, 2002; Seufert et al., 2003). Because of the quantum confinement effect, the small particle will create new energy levels and make some new applications possible, such as QD laser (Walter et al., 2002; Asryan et al., 2003; Marko et al., 2003) and quantum dot infrared photodetector (QDIP) (Ryzhii, 2001; Tang et al., 2002; Kochman et al., 2003). Thermal evaporation method is one of the easiest and earliest methods to produce nanoparticles. Crystalline gallium arsenide (GaAs) is a direct semiconductor with wide electronic and optoelectronic applications. Self-assembled GaAs QDs can be grown on InAs substrate by molecular beam epitaxy (MBE) and form anti-dot structure (Weiss et al., 1991; Leburton & Lyanda-Geller, 1997). The bandgap of GaAs is larger than that of InAs, therefore, it is

difficult to utilize the quantum confinement effect of the QDs. GaAs nanoparticles can also be synthesized by bottom-up approach (Kher & Wells, 1994), i.e., the chemical reaction of $(\text{NaK})_3\text{As}$ and GaCl_3 . In this paper, we demonstrated for the first time that the synthesis of GaAs spherical nanoparticles can be done by thermal evaporation method with Ga metal and GaAs wafer as the evaporation sources.

Experiments

The substrates were 7059 glasses, which were clipped on the sample holder. During the growth, the substrate can be cooled down by filling liquid nitrogen in the cold trap. Prior to the growth the 7059 glass should be immersed in $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ (3:1) for 30 min, rinsed in DI water for 10 min, and then blown dry with N_2 gas for cleaning organic matters. Two tantalum (Ta) boats filling with sources were connected to individual power supplies. Usually GaAs wafer which provides As source was broken to pieces and loaded in one

boat and gallium (Ga) metal was loaded in the other boat. The distance between the substrate and the sources were set from 8 to 13 cm. Then the chamber was evacuated to 10^{-5} Torr and purged with argon (Ar) three times to reduce the residual water vapor and oxygen. Cooled trap was filled with liquid nitrogen to lower the sample temperature to 77 K. The evaporation rates of Ga and GaAs source could be adjusted by controlling individual power supplies. After heating the boats for a fixed time, the shutter between the source and the substrate was opened for a certain time and the closed. Nanoparticles were deposited on the substrate.

Results and discussion

If only GaAs source is used, the arsenic evaporates much faster than the gallium due to its much higher vapor pressure at evaporation temperature. Only arsenic crystals will be formed, as shown in Figure 1a and b. The bigger polyhedrons are arsenic particles. The Raman spectra are shown in Figure 1c. The GaAs TO and LO phonon peaks locate at 260 and 299 cm^{-1} , respectively. It is clear that the LO and TO peaks of arsenic which locate at 197 and 244 cm^{-1} , respectively, are observed rather than GaAs. This indicates that there is too much arsenic present. However, if the As supply was insufficient such as the sample shown in Figure 2. The big spherical particles are gallium ball. And finally the optimal heating conditions to successfully synthesize the GaAs nanoparticles were found, i.e., the current flows through GaAs and Ga boats are 40 and 80 mA, respectively. The temperature of GaAs and Ga are 1250 °C and 1350 °C, respectively.

As shown in Figure 3 the SEM pictures (a–f) are those samples deposited at Ar pressure of 0.1, 0.3, 0.5, 1, 5 and 50 Torr, respectively. From these pictures some conclusions can be drawn. As can be seen in the Figure 3a–c there are no particles with distinct sphericity, the film looks like a paste. The paste-like films are amorphous, as indicated in their TED pattern. As a contrast at higher pressure larger than 0.5 Torr as shown in (d–f), the distinct particles become apparent. The critical point between the paste-like film and the distinct crystal particles is shown in (c) at the pressure of 0.5 Torr. The crystalline quality could be checked from

Figure 1. SEM pictures of GaAs and As particles grown with too much arsenic, amplified in (a) 10,000 times showing the small GaAs spheres, (b) 5000 times showing As crystals and (c) Raman spectra of GaAs and As particles.

Figure 2. SEM picture of Ga particles grown with too much gallium.

TED pattern. The diffraction rings are quite diffuse when nanoparticles were grown at low inert gas pressure (<0.3 Torr) and it means the film was amorphous. As the pressure becomes larger than 0.3 Torr the amorphous film gradually disappears and the ring pattern becomes sharper. Until the pressure goes to 1 Torr, the ring pattern becomes more distinct and the little bright spots besides the ring begin to appear. The crystalline quality had transferred from amorphous to crystalline film as the gas pressure is increased. Similarly the TED rings with bright spots shown in Figure 3e and f are further evidence that 3D large crystals are formed. As the pressure increases to 50 Torr, the crystalline particle would become huge polyhedron instead of sphericity, as shown in Figure 3f.

The spherical particles were primarily aggregated into long chain-like strands at a growth pressure of 1 Torr. The strands were linked together to form a web-like network. The reason might due to the fewer particles suspended in the chamber as grown at the lower inert gas pressure, and the cohesion and attractive force between particles were stronger than the force between inert gas molecule and nanoparticle. Thus as the crystal ball was forming, the dot would be going to stick to the first dot they touch due to their attraction. Then they land on the substrate in the

form of long chain-like or web-like strands. The relation between ring size and lattice constant could be detected by TED pattern. As listed in Table 1, the lattice constants of the nanoparticles are bigger when they are grown at a gas pressure larger than 1 Torr. Comparing the lattice constant of GaAs substrate, which was 5.65 Å, the lattice constant of nanoparticles grown by the thermal evaporation method was larger than GaAs

Figure 3. TEM pictures and TED patterns of GaAs nanoparticles grown at (a) 0.1, (b) 0.3, (c) 0.5, (d) 1, (e) 5 and (f) 50 Torr.

Figure 4. The average size of GaAs nanoparticles and its standard deviation as a function of the (a) growth pressure and (b) at low pressure <1 Torr.

Figure 5. Raman spectra of GaAs nanoparticles grown at the pressure of 0.1–50 Torr. Raman spectra of the GaAs substrate is also enclosed.

Table 1. The radius of TED (220) ring and lattice constant of GaAs nanoparticles grown at different pressure

Pressure (Torr)	TED-dia (cm)	Lattice constant (Å)
0.5	1.095	5.787
1	1.09	5.734
5	1.08	5.76
10	1.075	5.814
50	1.065	5.896
GaAs Sub	1.11	5.653

substrate. It is clear that while the growth pressure rises from 0.4 to 5 Torr, the average size of GaAs nanoparticles increases from 6 to 12 nm and standard deviation keeps almost the same (~ 2 nm) except for 0.5 Torr, as shown in Figure 4a and b. Besides, the average dot size increases from 18 to 100 nm and standard deviation also increases from 2 to 20 nm when the gas pressure rises from 10 to 50 Torr. Figure 5 displays the Raman spectra of GaAs nanoparticles prepared at different growth pressure, i.e., 0.1–50 Torr. While a good quality of film was formed, the Raman spectra would become more smoothly as in the case of 0.1 Torr sample. The reason why the TO phonon peak at 254 cm^{-1} was more obvious than the LO phonon at 275 cm^{-1} peak is attributed to the fact that when the Raman spectra were measured the sample surface have a hole bored by argon laser. Laser radiation broke the nanoparticles and burned the sample surface into a hole. So the phonons vibration is less strongly in longitudinal direction. Raman spectra of samples prepared at 0.3–1 Torr are similar. An observation of Figure 5 lowest curve, which is the Raman spectra of GaAs wafer, is known that a flat plateau located at approximate 200 cm^{-1} . If the crystalline quality of the sample surface is good, the hole is hardly bored and the TO peak will be more clear. As the inert gas pressure increases, the Raman spectra like the signal of the GaAs wafer would occur. The sample prepared at 50 Torr is most evident.

Conclusions

GaAs nanoparticles were successfully synthesized by thermal evaporation method using Ga and GaAs as the valence III and V sources. For GaAs nanoparticles grown at low inert gas pressure

(<0.3 Torr), the film was amorphous. As the pressure was increased to 0.5 Torr and beyond, spherical GaAs nanoparticles are gradually formed as evidenced by TEM and TED pattern. It is found that while the growth pressure rises from 0.4 to 5 Torr, the average size of GaAs nanoparticles increases from 6 to 12 nm and standard deviation keeps almost the same (~ 2 nm) except for 0.5 Torr. As the pressure increases to 50 Torr, the crystalline particle would become huge polyhedron instead of sphericity. From the Raman spectra, it is shown that the GaAs nanoparticles are dominant in the film.

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