Ion Beam Deposition of Quantum Dots from Colloidal Solution

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1. Introduction

Colloidal nanocrystalline semiconductor quantum dots with core/shell structure exhibit high photoluminescence quantum yield with very narrow emission spectra and broad photoluminescence excitation spectra. In addition, the CdSe/ZnS dots have color tunability from blue to red by controlling the size of the core. These properties strongly inspire to fabricate light emitting thin film devices by using the colloidal-synthesized quantum dots as luminescent active layers. However, there is challenge to fabricate the thin films with a vacuum process compatible with conventional semiconductor device manufacturing methods.

The major requirements in fabricating the luminescent thin solid films are that the quantum dot structure must be preserved, and the solvent and capping surfactant such as tri-n-octylphosphineoxide (TOPO) are totally removed during the film formation. The organics quench impact excitations by hot electrons in the so-called thin film inorganic EL devices or simultaneous injections of electrons and holes into the quantum dots in the case of LED devices. We developed a very low energy ion beam direct deposition (IBD) system for fabricating quantum dots structured thin films, and it is hereafter referred to as liquid-dispersed quantum-dots ion-beam deposition apparatus; LIQUID (RO-01EA, HOYA Corp.) [1] The developed system is high vacuum-consistent and can be connected with other vacuum processing chamber which generally utilized in the fabrication of light emitting devices. The core/shell structure of quantum dots is preserved while removing the organic molecules during the film deposition.

We previously reported a new fabrication technique of the organic free thin films from a solution of the surfactantcapped nanocrystalline quantum dots. In this paper, we show the energy spectrum of quantum dots ion beam, the cross-sectional transmission electron microscopy (TEM) image of the luminescent film and the photoluminescent spectra. It was evidenced that the nanocrystalline structure was preserved in the thin films.

2. Experimental Methods and Results

Liquid source solution

Liquid source solution of CdSe/ZnS core/shell type nanocrystals with an average core diameter of 2.4 nm giving photoluminescence peak at 530 nm, were used in the present experiments. Shell surface of the nanocrystals was terminated with tri-n-octylphosphineoxide ligand, and the dots were dispersed in a mixture solvent of 10% methylbenzene, 30% diethyl ether and 60% trichloromethane in volume. The concentration of the dots in the solution was approximately 0.1 mg/cm^3 .

Design and operation of the deposition apparatus

Schematic diagram of the LIQUID system is shown in Fig.1. It consists of five components for satisfying the above mentioned design concept; an electrospray ionizer, a supersonic jet emitter with a differential evacuation setup, a beam collimator consisted of cylindrical electrostatic lenses, an energy analyzer with deflection electrodes, and a deposition chamber. The source solution is fed to a microcapillary in air with atmospheric pressure. A positive DCvoltage of 1.2-2.0 kV is applied to the microcapillary with respect to the jet nozzle, which works as a counter ground electrode. Above the DC-voltage of 1.2 kV, formation of the Taylor-cone in the state of so-called cone-jet mode was clearly observed (Fig. 1 inset). The obtained well-shaped Taylor-cone contributes to formation of the emitted droplets of fine size and higher ion current yield. The typical beam ion current density was 10 pA/cm² measured through a Faraday cup under the applied voltage on the microcapillary of 1.85 kV and a flow rate of the source solution of $1.0 \times 10^{-3} \text{ cm}^{-3}/\text{min}.$



Fig. 1 Schematic picture of the LIQUID and photo image of tayler cone at the tip of microcapilally (inset).

The drift speed of the ions with a single positive charge traveling in air of atmospheric pressure under the applied electric field of 1×10^6 V/m can be estimated. Therefore, the

provided kinetic energies of the CdSe/ZnS nanocrystal and organic molecular (TOPO) ion are approximately estimated as 0.5 eV. These ions are the smallest case under consideration.

The ion beam is substantially accelerated on passing through the supersonic jet nozzle and on subsequent transit in the evacuated region up to the skimmer nozzle, which has a conical shape with an orifice on its vertex. The gas flow involving the ions gains a supersonic velocity. The speed of a paraxial portion of the free jet is calculated to be 1.1×10^3 m/s. The kinetic energy of the naked singly-charged nanocrystal ions with a diameter of 2.4 nm is estimated as 1.9×10^2 eV. For the nanocrystalline ion capped with several hundreds of TOPO ligands its kinetic energy amount to several kilo electron volts, taking presence of a reasonable amount of ligands at the surface into consideration.

Selection of the positively charged ions with appropriate mass-charge ratio is an essential step to fabricate thin solid films of the dots without the capping surfactant and solvent molecule. The ion beam is introduced to the Einzel configured electrostatic collimators. It was converged on a focal point in the energy analyzer, which is consisted of a couple of parallel planar electrodes. The energy analyzer was adjusted to select ions with energy of 6 keV, corresponding to a mass-charge ratio of 3.4×10^5 amu/e, because the energy spectrum of the ion beam has a maximum intensity around the ratio (Fig. 2). Under the condition, lighter ions and heavier ion complexes of QD, TOPO ligands, and/or organics are deflected to the areas outside the deposition region.



Fig. 2 Typical energy spectrum of the ion beam.

Finally, the refined nanocrystal ion beam was irradiated onto the grounded substrate. A soft landing is expected for the collision energy per atom of 0.1 to 0.4 eV/atom or less for singly-charged capped CdSe/ZnS crystals achieving appropriate collision strength for a dissociation of the surfactants from the surface of nanocrystals. The CdSe/ZnS crystals were deposited onto the single crystalline Si wafers. During the deposition process, the substrate temperature was kept at 423 K with a resistance heater to assist desorption of the TOPO ligands and residual solvent molecules from surface of the depositing nanocrystals. A cross-sectional high resolution TEM image of the deposited film formed using the nanocrystals with a nominal diameter of 2.4 nm is shown in Fig. 3. It is seen that the deposited film has a smooth planar morphology with a dense polycrystalline structure.



Fig. 3 Cross-sectional TEM image of a QD deposited film on a Si wafer substrate.

Photoluminescence (PL) and PL excitation (PLE) spectra for the deposited films and liquid source solutions were measured at room temperature using a conventional spectrophotometer (Fig. 4).



Fig. 4 PL and PLE spectrum of a QD deposition film.

3. Conclusions

The quantum confinement effect of the dots in the films is exhibited. It can be inferred here that the CdSe/ZnS nanocrystalline configuration and its optical functions are preserved in the organic-free thin films deposited by the newly developed IBD deposition technique (LIQUID process). It has ability to fabricate QD light emitting devices connecting with the high vacuum deposition process.

References

[1] S. Kobayashi, Y. Tani, and H. Kawazoe, Jpn. J. Appl. Phys. 46 (2007) L392.

Appendix

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