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Room temperature synthesized GaAs quantum dot embedded in SiO_2 composite film

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Abstract

Nano-composite films, consisting of GaAs quantum dots embedded in SiO_2 glass matrix, were fabricated and analyzed in terms of their structural, chemical, and optical properties. In order to fabricate uniformly dispersed GaAs quantum dots in the SiO_2 matrix, composite films consisting of alternate layers of GaAs and SiO_2 were deposited in the manner of a superlattice by radio frequency magnetron sputter deposition. In order to control the size of GaAs quantum dots the thickness of GaAs in individual layers was varied at a fixed GaAs total volume fraction. Transmission electron microscopy and X-ray photoelectron spectroscopy analyses revealed that GaAs quantum dots were in crystalline phase and in the form of a Ga–As compound. From optical absorbance measurements, absorption edges at visible wavelength band were determined and compared among composite films of varying GaAs nominal thickness. The amount of blue shift of the absorption edge increased with decreasing GaAs nominal thickness, i.e. quantum dots size. Band gaps of the composite films determined from Tauc plots and photoluminescence measurements exhibited a linear decrease with increasing GaAs nominal thickness. Large values of third-order non-linear optical susceptibility $\chi^{(3)}$ ($\sim 7.6\times10^{-14}\,m^2/V^2$ at 488 nm), which were believed to originate due to the state filling effect, were observed.

Keywords: Gallium arsenide; Quantum dots; Sputtering; Photoluminescence; Non-linear optical properties

1. Introduction

Semiconductor quantum dots (QDs) embedded in glass films, so called "nano-composite" film, have attracted a large amount of attention because they exhibit many useful optical and electrical properties stemming from quantum size effect. Furthermore, semiconductor QDs embedded in silica films provide not only a large nonlinear susceptibility, but have the additional advantages of low propagation loss, chemical stability, and low insertion loss in coupling to silica-based waveguides and fibers. Due to these attractive characteristics, glass films containing QDs have been studied extensively aiming potential applications for future optical and photonic devices such as QDs lasers, optical amplifiers, and optical switches [1–3]. In which excellent properties of ultrahigh integration, ultrahigh speed and ultralow power consumption are essential for successful application. Since the pioneering work by Jain and Lind [3], the impressive progress in the fabrication of low-dimensional semiconductor structures during the last decade has made it possible to produce various composite systems of semiconductor and silica glass. However, the majority of those studies have been centered on II–VI (CdS, CdSe–SiO_2), I–VII (NaCl, CuCl–SiO_2) compounds mainly due to the easiness of sample preparation demonstrated in the melt quenching–precipitation process and sputtering–recrystallization [4–6].

It was confirmed that composite films with III–V compound can be produced using the sputtering method. In the mid-1990s, Shi et al. [7] prepared GaAs–SiO_2 composite film with the co-sputtering technique at a substrate temperature 500 °C, and showed that a very large third-order optical non-linearity

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($\sim 5.4\times10^{-11}$ m^2/V^2) could be obtained for films with 10 nm diameter GaAs particles at 632 nm wavelength. Hirasawa et al. [8,9] reported that size-controlled crystalline QDs embedded in a SiO_2 matrix could be prepared successfully even at room temperature by the "digital" sputtering method, in which GaAs and SiO_2 films are alternatively deposited by carefully controlling the sputtering time. They showed that GaAs islands were in the form of crystalline phase at the initial stage of film growth and that the GaAs gradually changed to amorphous phase as GaAs grew into a continuous layer. However, no trial was attempted to examine the third-order optical non-linear property of such films deposited by an alternating sputter deposition method. The objective of this study was to quantitatively measure the structural, chemical, and optical properties of GaAs QDs–SiO_2 composite films prepared at room temperature by the alternating sputter deposition method and to obtain the third-order optical non-linear susceptibility $\chi^{(3)}$ of those composite films.

2. Experimental procedure

Size-controlled GaAs QDs embedded in SiO_2 composite films were deposited on fused silica glass and Si(100) substrates at room temperature by the alternate sputter deposition method in a multi-target radio frequency (RF) magnetron sputtering apparatus equipped with 2 in. GaAs (CERAC), and SiO_2 (Target materials INC.) targets. The RF power applied to the SiO_2 and the GaAs targets were 100 and 10 W, respectively. The substrates were positioned 8 cm away from the targets with an incidence angle of 23° to the substrate normal. The base pressure of the sputter chamber was 6.7×10^{-6} Pa, and the Ar gas flow rate and working pressure were 8 sccm and 0.67 Pa, respectively.

The composite films were alternatively deposited as follows. First, a continuous SiO_2 layer was deposited on the substrate by sputtering a SiO_2 target in an Ar atmosphere. Then GaAs was deposited on the top of SiO_2 to form GaAs QDs whose size was controlled by adjusting the deposition time required to produce a known nominal thickness of GaAs. Finally, the SiO_2 was deposited over the GaAs layer to bury the GaAs QDs. The same procedure was alternatively performed until the total thickness of the films reached 1 μm based on the deposition rate. The schematic diagram of a resultant composite film prepared by alternate sputter deposition method is illustrated in Fig. 1. In this study, in order to investigate the separate effect of GaAs QDs size on the optical properties of GaAs–SiO_2 composite while eliminating the effect of GaAs concentration, the volume fraction of GaAs in the composite films was fixed at 16.6% by adjusting the nominal thickness of GaAs and SiO_2. The nominal thickness of GaAs in 4 samples was 0.6, 1, 1.5 and 2 nm, and the corresponding nominal thickness of SiO_2 was 3, 5, 7.5 and 10 nm, respectively. In order to precisely control the deposition rate of GaAs and SiO_2, an automatic shutter system was installed between the targets and the substrates, and the on/off motion of the individual shutters was controlled by preprogrammed timers. The overall thickness of the samples was measured after deposition by the stylus profiler.

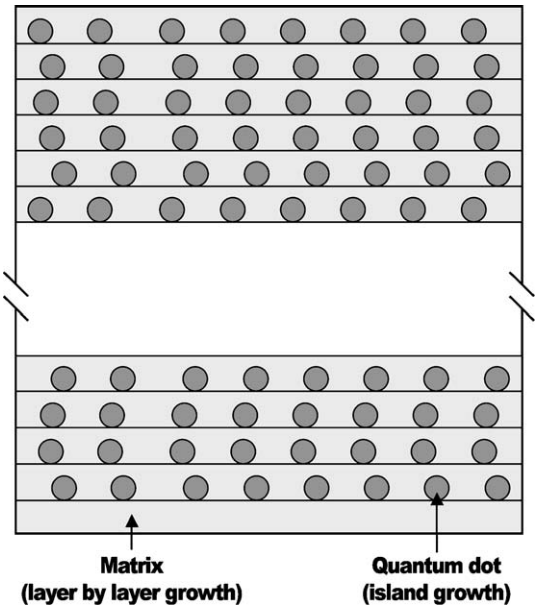

Fig. 1. A schematic diagram of a composite film prepared by alternate sputter deposition method.

The chemical state and crystal structure of GaAs QDs in the composite films was examined by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). XPS analyses were performed in an ESCALAB 250 system of VG Scientific Ltd., equipped with high-resolution (0.45 eV) hemispherical energy analyzer, with a base pressure of 1.3×10^{-7} Pa. For the XPS measurement, several steps of in situ Ar-ion etching were carried out prior to depth profile measurement, and then samples were excited with 1486.6 eV AlKα X-rays. The binding energies of Ga 2p3/2, As 2p3/2 emissions were measured and normalized with the Au $4f_{7/2}$ peak of the reference sample. To confirm the formation of crystalline GaAs QD, samples with single GaAs layer sandwiched in SiO_2 films were prepared on a Cu grid with ultra thin carbon film and analyzed by JEOL 4000EX(II) high-resolution TEM operated at 400 keV with a LaB_6 filament. The composition, i.e. the volume fraction of GaAs, of the samples was estimated by Rutherford backscattering spectrometry (RBS) analysis, in which 2 MeV He^{2+} ions were measured at a scattering angle of 170°.

The optical absorption of composite films was measured from 200 to 1100 nm at 1-nm increments with a spectrophotometer (Lambda 35, Perkin-Elmer) at room temperature. The photoluminescence (PL) spectra of composite films were measured at 18 K from 380 to 600 nm at 0.3-nm increments. The samples were mounted on a cold finger of closed-cycle He cryostat and excited by He–Cd gas laser (325 nm) at a power of 1 mW with beam spot size of 100 μm.

Non-linear optical properties were studied by the single beam *Z*-scan method [10]. For the *Z*-scan measurement, a continuous Gaussian beam of Ar^+ laser (488 nm, 514.5 nm) with various irradiances was focused by an objective lens of NA 0.1. Both the open and the closed aperture *Z*-scan experiments were performed with scan range of ±0.5 mm around the focal point.