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Growth of Nb_2O_5 quantum dots by physical vapor deposition

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ABSTRACT

The crystalline quantum dots of Nb_2O_5 in the range 1–20 nm have been grown by vacuum thermal evaporation using the bottom-up approach of early nucleation and growth stage. The dot sizes were controlled by growth time for an optimized constant molecular flux rate of growth. The dots were characterized by TEM and UV/Vis absorption spectroscopy. The variation of optical band gap of dots scaling with inverse square of their size demonstrates the quantum confinement effect in the dots. The reduced mass of electron–hole pair (exciton) was determined to be 0.532 m_e from this behavior.

1. Introduction

Nanomaterial research has sparked off new enthusiasm in material scientists for exploring novel growth methods either new or creatively manipulated, modified old techniques, etc., for the growth of various materials with nanometer size, especially the quantum dots. 'Smaller is better' has been the essence and core concept of nanomaterials growth. However, the growth of quantum dots of various materials has been particularly interesting from the view of both basic and applied research. In general, both bottom-up and top-down approaches have been explored for quantum dot growth, however, the bottom-up approach has been more common, popular and consistent. Many of the existing and old methods of materials synthesis have been adopted with necessary modifications for this purpose. Very surprisingly, the vacuum physical vapor deposition, in particular, the thermal evaporation technique seems to be ignored in this race of growth methods of quantum dot. Thin film growth has greatly contributed to the modern development of devices and the related technologies. Thermal evaporation has advantages of being simple, adoptable for any material, clean, economical, and capable of growing on any type of substrate and the likes. The initial stage of film growth (early nucleation and growth stage) by physical vapor deposition can also be utilized and adopted as a "bottom-up" approach of growth technique. This is because; the atomic/molecular vapor produced by the evaporation of the desired bulk material condenses on the substrate to form the film within a reasonable time. The process of vapor condensation on substrate is not as simple as it looks to be. It depends on many parameters of substrate (such as type of substrate and substrate temperature) and the evaporant (such as melting point and vapor pressure). The condensation on substrate should proceed with assembling of molecules, from few to large numbers, with increasing size of the condensate with time after the formation of critical nuclei. Therefore, it is not difficult to imagine that the size of the condensate can be controlled through growth time. Therefore, we attempt to address these issues, to demonstrate the adoptability of thermal evaporation for quantum dot (QD) growth comprehensively. Once the possibility of growth is established, the various possible applications of the quantum dots will follow with the necessary modification of the growth method.

We choose to grow quantum dots of niobium pentaoxide (Nb_2O_5) which is an emerging multi-functional material in recent years. It can be used for various applications in optoelectronics [1,2], optical devices, gas sensing, catalytic activity, ionic batteries and also electrochromic devices [3–5]. Also, Nb_2O_5 happens to be thermodynamically most stable among Nb's all the other different oxide stoichiometries [6]. Interestingly, Nb_2O_5 can exist with various crystal structures: monoclinic, orthorhombic, tetragonal and hexagonal as evident from the various JCPDS data from the literature. This makes it more interesting and motivated to explore Nb_2O_5 in its various structures in different forms. Furthermore, the properties of Nb_2O_5 strongly depend on its synthesis procedure due to which various synthesis routes and methods are being explored for both its bulk and nano scale forms. There have been some reports regarding the growth of nanotubes and nanoparticles [7–9] of Nb_2O_5 by chemical routes in the literature.

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2. Materials and methods

The Nb_2O_5 QDs were grown on very thin glass substrates (1.5 cm × 1.5 cm × 100 mm) at room temperature by thermal evaporation using tungsten basket. The starting material was stoichiometric and high purity (99.998%) Nb_2O_5 powder (Alfa Aesar) and it was palletized for avoiding spattering during evaporation. All the samples were grown at a base vacuum better than 10^{-6} Torr using turbo molecular pump. The deposition rate (2.7×10^{21} molecules/s) was optimized for the size control and to grow uniform good quality dots. The deposition rate was calculated from the rate of mass deposited on the quartz crystal of the thickness monitor. Pre-polymer coated TEM grid was kept along with the glass substrate during the growth. The dot size was varied by varying the deposition time. The constant deposition rate was ensured and monitored during the growth by a quartz crystal monitor (HIND HIVAC-Quartz Crystal Thickness Monitor Model – 101). The structural and size analyses of the dots were carried out by high-resolution transmission electron microscopy (HRTEM) using a Technai G20-s twin microscope (operated at 200 kV). The optical absorption measurements were carried out using a uv/visible spectrophotometer (HITACHI U-3900H). All the measurements in the present work were carried out at room temperature (~300 K).

3. Results and discussion

The structure and sizes of various dots grown at different growth durations were determined using HRTEM. Hereafter each sample will be identified and labeled by the growth time indicated in the figures or captions. Some representative images are shown in Fig. 1. In the figure, only one representative selected area electron diffraction (SAED) image is shown. However, SAED images of all the samples were similar with more or less number of spots from different (*hkl*) reflections. The appearance of diffraction spots clearly indicate the crystalline phase of the quantum dots formed. The *d*-spacings of the spots were determined by the software provided with the electron microscope. These *d*-spacings match best with JCPDS No. 72-1484 for the tetragonal phase. We have also taken the XRD (not shown here due to limitation) of the Nb_2O_5 powder used for the dot growth which matches best with JCPDS No. 72-1484 indicating the same tetragonal phase of the starting material as that of the quantum dots formed. We can see from figure, the progressive growth of various dot sizes with growth duration. However, it should be noted that the dots are almost like monodispersive with narrow dot size distribution for small dots of mean diameter up to 5 nm. The dot size (dot diameter) distribution starts widening for larger dot sizes than 6 nm which is also evident from the figure as per the micrograph of 210 s. This is qualitatively quite consistent with the predictions of the nucleation and growth theories. In the present study, we have grown Nb_2O_5 QDs of average (mean) dot size varying from 1 to 20 nm and the three micrographs in Fig. 1 depict the average dot size of 1, 3 and 12 nm. We represent the mean dot diameter by *d* (nm) and the size distribution by $(-n_1, d, +n_2)$ where n_1 and n_2 are the numbers (nm) to be subtracted or added to *d*, respectively, to get the lower and upper limits of the size distribution associated with each *d*. The mean diameter *d* represents the diameter of the 70–80% dots in the sample. We have grown dots of $d=1$ nm with $(-0.2, 1, +0.5)$, $d=1.5$ nm with $(-0.8, 1.5, +1)$, $d=2$ nm with $(-1, 2, +1.5)$, $d=3$ nm with $(-1.5, 3, +2)$, $d=5$ nm with $(-2, 5, +2.5)$, $d=9$ nm with $(-4, 9, +6)$, $d=12$ nm with $(-6, 12, +8)$ and $d=20$ nm with $(-9, 20, +15)$.

Detailed Raman and FTIR studies were also carried out on these samples (not shown here due to journal size constraint) which reveal that the dots formed are of same composition and phase of the starting powder.

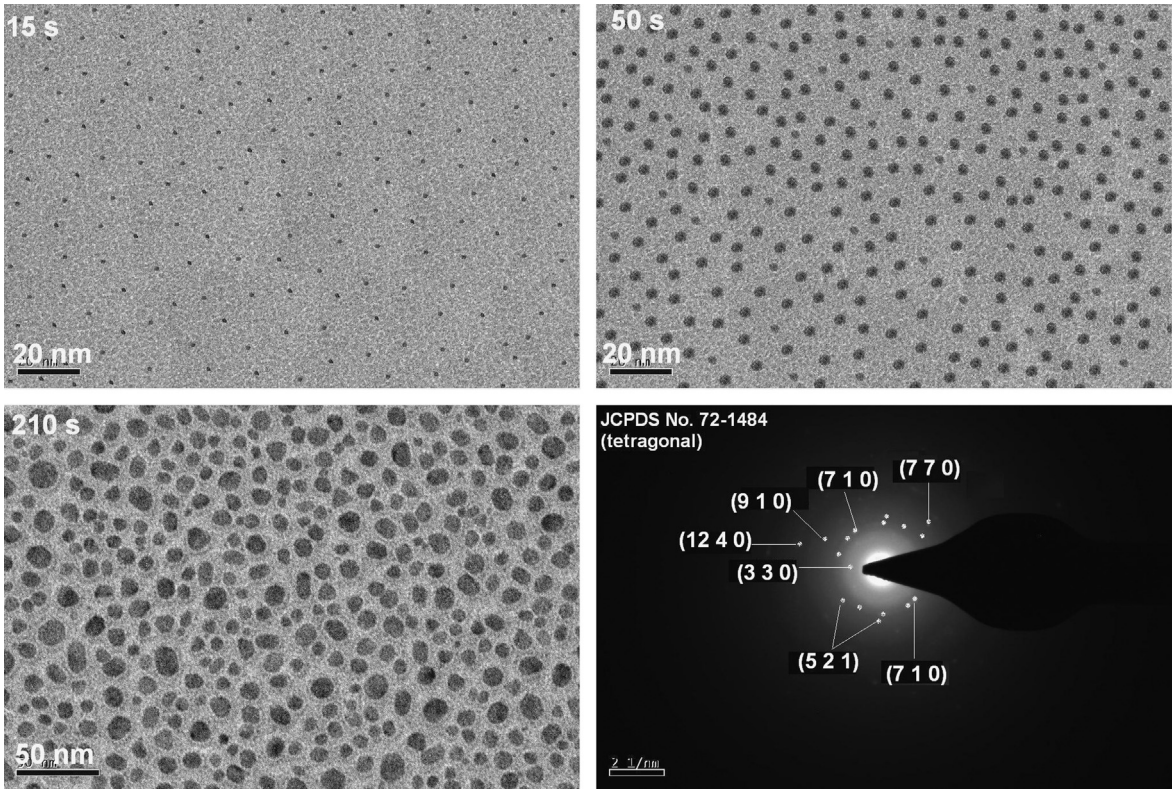

Fig. 1. TEM images of Nb_2O_5 QDs grown with a constant flux rate of 2.7×10^{21} molecules/s at different growth durations as indicated on each micrograph. Selected area electron diffraction (SAED) image of one representative sample is also shown in the figure. The contrast of the white diffraction spots are enhanced for better visibility.