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Blue-luminescent hafnia nanoclusters synthesized by plasma gas-phase method

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ABSTRACT

We report the preparation of a blue luminescent metal oxide, hafnia nanoclusters (NCs), via plasma gas-phase condensation deposition method. The as-synthesized hafnia NCs show a narrow size distribution with a mean cluster size of $d = 6.5$ nm and possess a tetragonal crystal structure that was rarely obtained at room temperature via traditional synthetic methods. The as-prepared hafnia NCs are surface clean and have high purity because of vapor condensation and cluster growth in the high vacuum and dry system. It is suggested that the blue luminescence should originate from oxygen defects in the tetragonal hafnia NCs.

1. Introduction

Hafnia (HfO_2), a very important metal oxide, has attracted active attentions for its diverse practical applications in optical coatings [1], catalysts [2], gate dielectric [3,4], etc. It is worth to note that pervious work mainly focused on hafnia bulk, powders and films, the preparation of hafnia NCs have seldom been reported [5,6] because of the formidable challenges associated with the synthesis of nano-structures with controlled dimensions and crystal phases [7]. Hafnia NCs in the rare reports were prepared by solution-based approaches, such as nonhydrolytic sol–gel process [5,6]. Moreover, the synthesized NCs exhibited a broad size distribution or capped by solvents or organic ligands. Thus, synthesis of very small hafnia NCs with narrow size distribution and high purity is still a great challenge. Plasma gas-phase synthesis is a very powerful technique to prepare NCs of metals, alloys and metal compounds with controllable sizes and compositions. Especially, the advantage of this technique is that vapor condensation and cluster growth in the high vacuum and dry system can eliminate impurity and hydrolysis problems which are associated with aqueous methods.

Motivated by exploring the fundamental nature of pure hafnia nanoparticles, it is imperative to synthesize hafnia NCs that have clean surfaces, high purity and narrow size distribution. In this work, we employed plasma-gas-condensation cluster deposition (PGCCD) method to prepare hafnia NCs. We discovered that the prepared hafnia NCs with a tetragonal phase exhibit a blue luminescence under 365 nm excitation.

2. Experimental

2.1. Fabrication of hafnia NCs

A schematic of the plasma-gas-condensation cluster deposition (PGCCD) system is revealed in Fig. 1. Prior to deposition, the system was pumped down to 8.0×10^{-4} Pa. Two high purity Hf targets (99.99%) with a diameter of 72.6 mm were fixed oppositely. On deposition, ultrapure (99.999%) argon gas of 200 sccm was introduced into the sputtering chamber, and the chamber pressure was kept at 60 Pa. Ultrapure (99.999%) oxygen gas of 10 sccm was introduced into the cluster assembling chamber. The dc sputtering source was applied to produce high density metal Hf vapor. The sputtering voltage and current were fixed at 300 V and 0.8 A, respectively. NCs nucleated in a higher working pressure (60 Pa) compared with conventional magnetron sputtering and grew in the space between the target and the first nozzle. Then the formed Hf NCs and argon gas were extracted twice (through second nozzle and third nozzle) for preventing the NCs from further growth. The Hf NCs reached the nanocluster assembling chamber filled with oxygen and argon mixed gas atmosphere and were oxidized into hafnia NCs, and finally the hafnia NCs softly landed onto the substrate in the nanocluster assembling chamber with a chamber pressure of 3.0×10^{-2} Pa. The whole flying process of NCs was driven by pressure gradient.

2.2. Sample characterization

The samples for the measurements of X-ray diffraction (XRD), UV–vis absorption spectra, Raman spectra, photoluminescence (PL) and PL excitation (PLE) spectra were deposited on quartz glasses. The samples for SEM measurements were deposited on Si (1 0 0). XRD patterns of hafnia NCs were performed by a Panalytical X'pert PRO X-ray diffractometer using Cu Kα radiation at 40 kV and 30 mA. Raman spectra were measured by Renishaw Invia Raman Microscope with an excitation wavelength of 532 nm, the laser power is 30 mW, and exposure time is 30 s at 2 accumulations of the spectra. Transmission electron microscopy (TEM) examination was carried out using a JEOL-2100 with an accelerating voltage of 120 kV.

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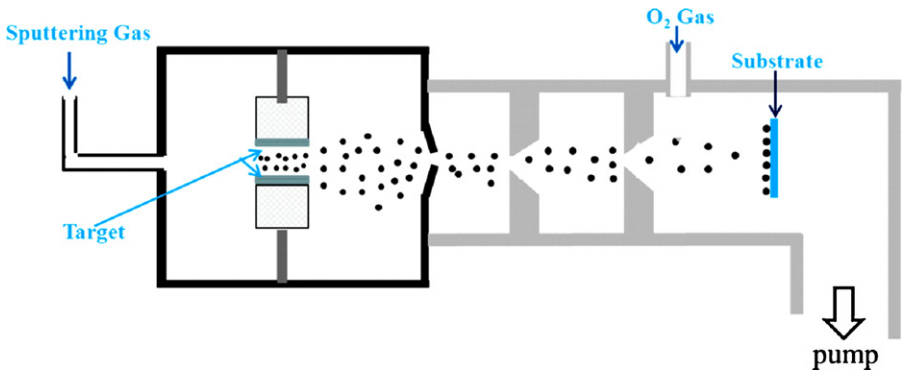

Fig. 1. Illustration of the plasma-gas-condensation cluster deposition system (PGCCD) and the formation process of hafnia NCs in the system.

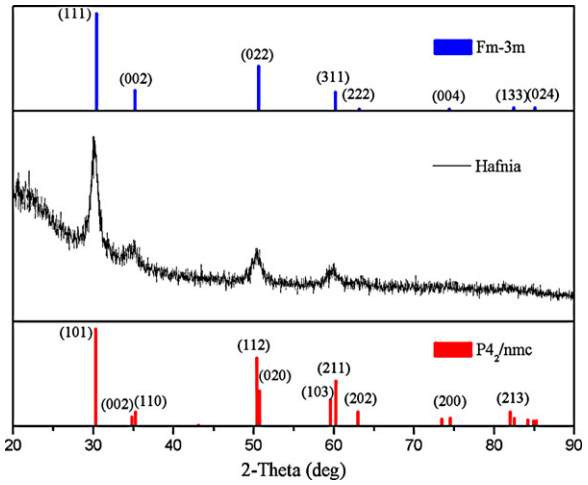

Fig. 2. XRD pattern of the hafnia NCs (the top and bottom images are cubic and tetragonal phase, respectively).

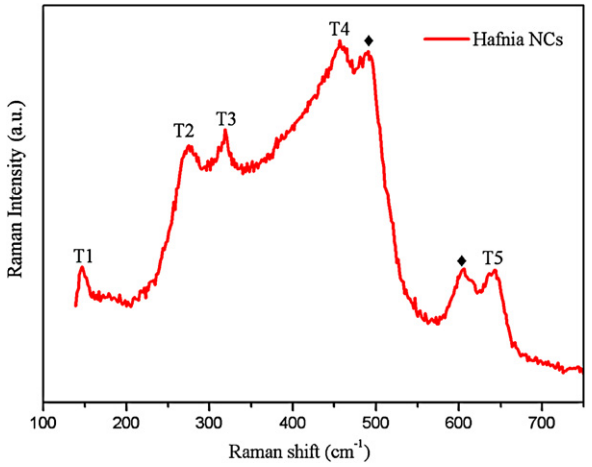

Fig. 3. Raman spectrum of hafnia NCs deposited on quartz glass. The peaks labeled with ♦ belong to quartz glass.

High-resolution TEM (HRTEM) measurements were carried out on a JEOL-2100 with an accelerating voltage of 200 kV. Samples for TEM observation were prepared via the direct soft-landing of hafnia NCs onto carbon-coated copper grids. The nanocluster size and size distribution diagram were obtained by measuring more than a hundred individual hafnia nanoparticles carefully. UV–vis absorption spectra were recorded on a Varian Cary 5000 recording spectrometer. PL and PLE spectra were obtained on a Hitachi F7000 fluorescence spectrophotometer equipped with a 150 W Xe lamp as the excitation source. All measurements were carried out at room temperature.

3. Results and discussion

Similar to ZrO_2, hafnia bulk can adopt three different crystal structures at ambient pressures, i.e., monoclinic (~<1720 °C), tetragonal (1720–2600 °C) and cubic (>2600 °C) phases. Tetragonal and cubic phases cannot be quenched to room temperature, although these phases (when stabilized by doping) are far more important in technological applications than the low-temperature phase materials [6]. Generally, the stabilization of tetragonal or cubic phase at room temperature can be achieved via incorporating divalent and trivalent cation dopants or controlling grain size, which both introduce oxygen vacancies that stabilize tetragonal or cubic phase [8].

Fig. 2 shows the XRD pattern of the hafnia NCs. The diffraction pattern reveals that the hafnia NCs are formed in either tetragonal or cubic phases, rather than monoclinic phase which is stable at room temperature. In order to identify whether it is tetragonal or cubic, Raman spectroscopy was applied to probe the vibrational and structural properties of the hafnia NCs. Fig. 3 shows the Raman spectrum of the hafnia NCs deposited on quartz. The peaks around 146, 276, 318, 458, 640 cm^{-1} (labeled T1–T5) match well with the results reported in the literature for typical signature of tetragonal hafnia [6,9–11]. Meanwhile, characteristic peaks around 322, 620, and 711 cm^{-1}, which were detected in yttrium stabilized cubic hafnia [12], are not observed in our hafnia NC samples. Therefore, the results indicate that the hafnia NCs should be formed predominantly in the tetragonal phase. The broad peaks can be attributed to very small particle size and introduced oxygen vacancies [9,12]. The peaks at 490 and 603 cm^{-1} (labeled ♦) are contributed to quartz substrate.

Fig. 4(a and b) is the low-magnification and enlarged TEM images of the as-prepared hafnia NCs, respectively. All the TEM images reveal that the NCs are spherical and randomly distributed. The mean particle size is 6.5 nm, and the standard deviation ($\Delta D/D$) is less than 8%, indicating a narrow size distribution. HRTEM image (Fig. 4(c)) from a single hafnia NC demonstrates that the NC is well-crystalline, and the measured lattice fringe of 3.03 Å corresponds to the distance of (1 0 1) crystal planes of tetragonal hafnia. Fig. 4(d) shows the selected area electron diffraction (SAED) pattern of the corresponding hafnia NCs. All the diffraction rings can be indexed to tetragonal hafnia. Fig. 4(e) is the SEM image of hafnia nanoparticle-assembled film with a thickness about 500 nm deposited on Si (1 0 0). Energy-dispersive X-ray (EDX) analysis of numbers of NCs shows that only Hf and O were contained (Fig. 4(f)). The above results highlight the advantage of the plasma gas-phase synthetic technique in forming contamination-free NCs with narrow size distribution.