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Silica nano-rings and nano-hollows: Preparation and UV photoluminescence emission

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ABSTRACT

By annealing fused silica coated with ultra-thin Ag film, silica nano-rings and nano-hollows were prepared on the substrate. The Ag nano-particles attached on the wall of nano-hollows or embedded in silica were confirmed with energy dispersive spectroscopy and transmission electron microscopy. Besides the well-known characteristic stretching bands of silica, three novel stretching bands around 1579, 1320 and 270 cm^{-1} were found in the annealed Ag-coated silica by Raman scattering spectroscopy, which have been attributed to the O_2 in ground state, O–O and metal–oxygen stretching bands, respectively. The formation mechanism of nano-rings and nano-hollows has been discussed based on the experimental results. An ultraviolet photoluminescence emission of 360–370 nm from annealed Ag-coated silica was found when the excitations were 230 nm and 280 nm or longer. The possible photoluminescence emission mechanism has been discussed, which suggests that oxygen excess defects are responsible for the photoluminescence emission, and photoexcitation occurs in the silica as well as in Ag^+ ions.

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1. Introduction

Recently, the preparation and application of meso- or nano-sized rings and hollows structures, nano-rings (NRs) and nano-hollows (NHs), has become an important research field, since NRs and NHs showed many unique optical, electric, magnetic, and catalytic properties [1–3]. The tunable optical properties of ring-shaped materials can also be achieved by varying the diameter and thickness of the ring [4] and by patterned structures of NRs and NHs [5]. On the other hand, filling the NHs with functional materials, quantum confined structures and their associated quantized effects may be demonstrated in a variety of host structures such as plastics and glasses [6–8]. The fabrication of meso- and nano-porous silica has been extensively investigated, since porous silica is one of promising materials for the development of new optical sensors and luminescent devices [9,10], in addition to an ideal host material for the study of chemical and physical behavior of confined molecules [11,12]. However, the researches of preparing meso- and nano-sized NRs and NHs structures in silica have made few progresses because of the thermal and chemical stability of SiO_2. Even if the conventional lithographic technique has been used [13], there are also some drawbacks, such as low throughput due to its long exposure time and a sophisticated equipment system.

In the present study, we report that with the reactions between Ag and silica at high temperature the NRs and NHs structures can be formed on fused silica substrates. Furthermore, we have investigated extensively the ultraviolet PL emission of 360–370 nm from the annealed Ag-coated samples. The possible mechanism of PL emission and the effect induced by Ag nano-particles are discussed.

2. Experimental procedure

The experimental description is given briefly: A conventional tube furnace was used in the present work. Commercially purchased optical fused silica wafers, 1 mm thickness, were used as the substrates. After ultrasonically cleaning with acetone and ethanol to get rid of the surface contamination, the silica wafers were coated with an ultra-thin Ag film, 10 nm thickness, by sputtering

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the Ag target. The Ag-coated fused silica was then put onto a quartz boat and horizontally transferred into the furnace. The annealing process was carried out in pure N_2 atmosphere under ambient pressure. The temperature of the furnace was raised to 1000 °C within about 30 min and then maintained at that temperature for 40 min to let Ag react with the silica substrate. After the furnace cooled down to room temperature, the annealed sample was taken out of the furnace for further characterization.

The surface morphology of annealed silica substrate was characterized with scanning electron microscopy (SEM FEI Sirion with EDS attachment and JEOL JSM-5900LV). The detailed information about the morphologies and structures of NRs and NHs was studied with high resolution transmission electron microscope (HR-TEM FEI-F20 with EDS attachment and JEOL 2010) by cross-section transmission electron microscopy (XTEM). The micro region chemical composition study was carried out with EDS attachment. The characterization of Raman scattering spectroscopy were conducted by a Raman spectroscope with a 633 nm HeNe laser source (Renishaw InVia, lateral spatial resolution <1 μm and spectral resolutions 1 cm^{-1}). The PL characterizations were performed using a spectrophotometer with a Xe lamp (HITACHI F-4500, spectral resolution 1 nm).

3. Results

Fig. 1(a) illustrates the SEM image of as-prepared NRs on the substrate. The SEM characterization reveals the formation of a dense ring-shaped nanostructure on the surface of the annealed Ag-coated silica substrate. According to the SEM image, we can estimate that the outer and inner diameters of NRs are 50–100 nm and 10–20 nm, respectively. The width of the NR is about 20 nm. The composition characterization conducted with the EDS attachment on the SEM reveals that there is no detectable Ag on the surface. Structure and composition of NRs were studied in detail by cross-section high magnification transmission electron microscopy (XTEM) and the EDS attachment. The composition characterization conducted with the EDS attachment on the TEM reveals that the NRs are free from Ag, which is consistent with the result mentioned above. A rational speculation might be that the residual quantity of Ag is too small to be detected with the EDS. From the XTEM image, as seen in Fig. 1(b), we can find a typical volcano-like ring-shaped cross-sectional image of NRs. The height of the NRs is about 10 nm. The most interesting finding is that there is a NH of about 150 nm depth under each NR. In addition, there are many black dots in the NHs. The EDS characterization, as shown in Fig. 1(c), reveals that these black dots are Ag. By means of XTEM, we have also found that some of the Ag atoms diffused into the silica substrate and aggregated to form Ag nano-particles of 3 ~ 5 nm diameter, as seen in Fig. 1(d). The depth of Ag nano-particles in the silica was about 1–2 μm according to the TEM image.

In order to further elucidate the formation mechanism of the silica NRs and NHs, the evolution of surface morphology with annealing time at 1000 °C was investigated. In samples annealed at 1000 °C for 10 min, a few of Ag nano-particles and silica NRs were observed, as shown in Fig. 2(a). It is noteworthy that some Ag nano-particles were located at the centers of NRs. After annealing at 1000 °C for 20 min, the density of Ag nano-particles decreased and the number of silica NRs increased on silica substrate from Fig. 2(b). A few of Ag nano-particles also remained at centers of silica NRs. After annealing at 1000 °C for 40 min, the dense silica NRs formed and Ag nano-particles disappeared from the surface, as shown in Fig. 1(a), indicating that the silica NRs were formed after the Ag nano-particles reacted with SiO_x and sank into the substrate during thermal annealing process.

The Raman spectra of the un-annealed bare fused silica and annealed Ag-coated fused silica are shown in Fig. 3 as curves a and b, respectively, in which all the well-known characteristic bands of silica appeared. The 450 cm^{-1} band is assigned to a Si–O–Si bending mode, the signals at 804 and 1065 cm^{-1} to Si–O–Si symmetric and asymmetric stretching modes, respectively, and two bands at 490 and 603 cm^{-1} to four- and three-fold Si–O rings [14]. Compared with un-annealed bare fused silica, the Raman scattering background of the annealed Ag-coated fused silica is obviously in-

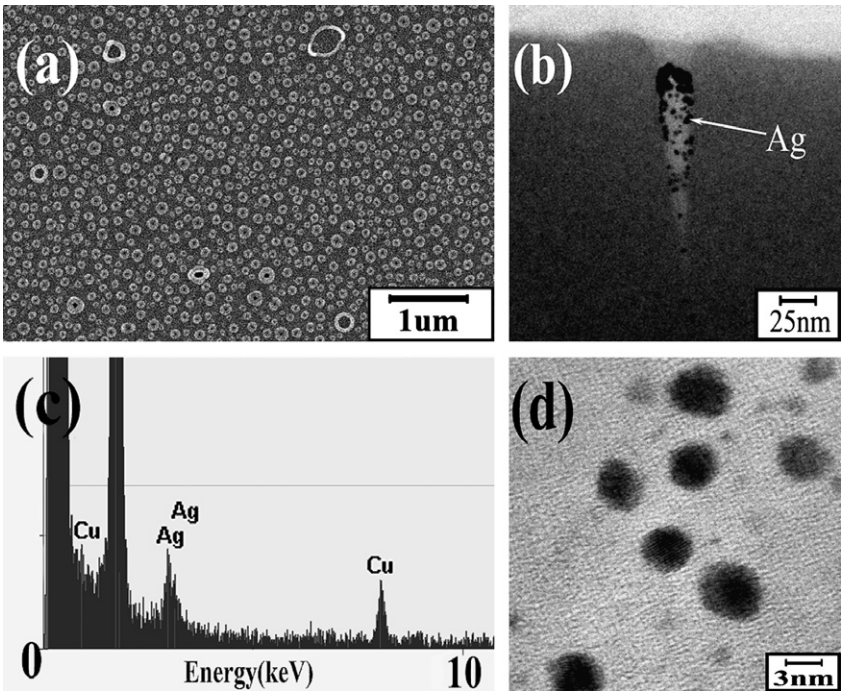

Fig. 1. SEM image (a) and XTEM image (b) of the as-prepared NRs and NHs on fused silica and EDS spectrum (c) corresponding to the black dots marked by arrow, which indicates that the black dots pointed out are Ag. (d) XTEM image of Ag nano-particles inside the silica.

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