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From photoluminescence emissions to plasmonic properties in platinum nanoparticles embedded in silica by ion implantation

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ABSTRACT

We have studied photoluminescence emission and optical absorption from platinum nanoparticles (Pt-nps) embedded in a silica matrix obtained by ion implantation. The Pt ions were implanted at 2 MeV and the nanoclusters were nucleated after thermal treatment at 600, 800, and 1100 °C under two different atmospheres: argon gas and a reducing atmosphere compound of H_2 and N_2. The luminescent spectrum is broader (400–600 nm) and is peaked at 530 nm, but its intensity decreases as the annealing temperature increases. However, at high annealing temperatures, a Mie resonance at 220 nm emerges in the absorption spectrum. We then observed a transition between two optical properties in a system of Pt-nps embedded in silica: from molecule-like properties such as photoluminescence emission to localized surface plasmon absorption.

1. Introduction

Platinum nanoparticles (Pt-nps) have been extensively studied for their application as a catalytic material [1–3]. However, research into other properties such as optical absorption and fluorescence emission has received less attention. In recent years, some authors have reported that Pt nanoparticles (Pt-nps) with a size less than 2 nm and synthesized by chemical methods present a strong photoluminescence (PL) emission [4–11]. These works report that the PL spectrum from Pt-Ncs is broad (from 350 to 500 or from 450 to 800 nm) and has a peak between 400 and 550 nm. Nanoisland films made of Pt-nps also have been reported to present a micro-photoluminescence emission in the visible light region [12]. The origin of these emission properties in Pt-nps, as well in other noble metal such as Ag and Au, have been attributed to a discretization of the energy band levels as a consequence of the reduced size of the nanoparticles [13–16]. This means that for these dimensions metal nanoparticles exhibit a molecule-like behavior. When metal nanoparticles grow, their electron energy levels form a continuum density of states, and then molecule-like properties, like fluorescence, tend to disappear [15–17]. A continuum density of states can support the characteristic plasmon Mie resonance due to collective oscillation of conduction electrons, generally observed in 2 nm metal nanoparticles or greater in size [18]. Plasmon Mie resonance of Pt-nps, synthesized by chemical methods [19] and colloidal lithography [20] are reported to exhibit a broad band absorption spectrum with a peak in the ultraviolet range (230–400) for nanoparticles with sizes of 30–70 nm. On the other hand, even though Pt-nps embedded in a silica matrix by ion implantation have also been synthesized [21–23], there are no studies about their optical properties to date. Much effort has been devoted to studies on optical properties of metal nanoclusters (mainly made of Au and Ag) embedded in a solid matrix because of the wide range of possible applications in the field of nonlinear optics, nanophotonics, and optical communication technology [24–26]. In this work, we have obtained, by metal ion implantation, ultra-small Pt-nps embedded in a silica matrix (SiO_2). We will show that, after a proper thermal annealing, we can observe a strong emission of PL from the Pt-nps embedded in the silica matrix. Also, we show that increasing the average size of the Pt-nps formed inside the matrix, by using different temperatures for the annealing, the PL intensity is quenched, but it is now possible to observe a characteristic plasmon Mie resonance of the Pt metal nanoparticles.

2. Experimentals

Platinum nanoparticles were synthesized by metal ion implantation in a high purity silica matrix (suprasil 300) of $20 \times 20 \times 1$ mm. The Pt ions were implanted at room temperature at 2 MeV using the 3 MV Tandem accelerator (NEC 9SDH-2

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Pelletron) facility at the Instituto de Física of the Universidad Nacional Autónoma de México (IFUNAM). The fluence used was 7×10^{16} Pt-ions/cm^2. Once the silica was implanted with Pt ions, it was cut into six smaller pieces. Three of these pieces were heated at 600, 800 and 1100 °C, each of them under argon gas (Samples Ar-600, Ar-800, Ar-1100), and the other three pieces were heated at the same temperatures but under a reducing atmosphere (RA) compound of 50% of H_2 and 50% of N_2 (Samples AR-600, AR-800, AR-1100). The concentration profile of the implanted Pt was calculated using the SRIM code [27,28], and was corroborated experimentally by means of Rutherford Backscattering Spectrometry (RBS) [29] using 2 MeV $^4He^{++}$ beam. We used the RUMP code to calculate the concentration profile of the implanted ions. For all the sample studies in this work the Pt implanted ions were distributed in the range 250–900 nm under the silica surface with a peak atomic concentration of 3.2 at% at 600 nm.

Photoluminescence (PL) measurements were performed at room temperature and at excitation wavelengths of 250, 310 and 355 nm using ps pulses, at a frequency repetition rate of 10 Hz from a combined laser system PL2143A+PG401/SH by EKSPLA. The PL signal was collected by a 1000 μm optical fiber and detected by an Ocean Optics USB2000+ spectrometer. The optical absorption of all the samples was measured by means of a Varian Cary 5000 UV–vis spectrophotometer. Some PL spectra were obtained using 250 nm as an excitation wavelength to see a possible PL from defects produced in the silica matrix after ion implantation [30–32]. Pt-nps were observed by using a FEI TECNAI F30 Transmission Electron Microscope (FEG-TEM 300 kV) in scanning mode (STEM) with a HAADF detector (Z-contrast).

3. Results and discussion

Once Pt ions are implanted in the silica matrix we can observe luminescent emission bands from silica defects state. To observe these emission bands the sample is excited with a laser wavelength range between 230 and 300 nm. In Fig. 1 the emission bands from a piece of silica implanted with Pt ions at 2 MeV are shown. These emission bands have been observed and extensively studied before [30–36].

As shown in the inset in Fig. 1, the excitation wavelength was 250 nm just in the peak of the absorption band observed at 250 nm. It has been determined that B_2 defects in silica have an absorption band peaked at 248 nm and a halfwidth about 15 nm [31–33]. Therefore, the absorption band observed at 250 nm could be ascribed to the presence of B_2 defects in silica induced by Pt implantation. On the other hand, NBOHC and POR defects have an absorption band in almost the same spectral region. Both defects have an optical absorption peak at 258 nm and a halfwidth about 55 nm and 44 nm for NBOHC and POR, respectively. When these defects are excited with a laser wavelength within their optical absorption bands it is possible to observe their characteristic PL emission [34–40]. All the emission bands in Fig. 1 can be related to defects state produced in the silica matrix. A deconvoluted curve allows us to observe five differentiated emission bands at 289, 450, 489, 550 and 650 nm. The ultraviolet (289 nm) and blue (450 and 489 nm) emission bands are produced due to the presence of B_2 defects [31–33]. Peroxide Radical Oxygen produces the green emission band at 550 nm [34–38]. And the red emission band at 650 nm is produced by Non-Bridged Oxygen Hole Centers [32,39,40].

It is well known that defects states in a silica matrix can be passivated by means of a thermal annealing under Hydrogen or Nitrogen containing atmosphere. Consequently, the luminescent emission from them is quenched [30,41,42]. Fig. 2 shows the absorption spectrum from two silica samples implanted with Pt ions which were then thermal annealed at 600 °C for 1 h under two different atmospheres: argon and RA. The optical absorption spectra of as-implanted and virgin silica is also shown for comparison.

The absorption band around 250 nm, related to the presence of B_2 silica defect states, is not present in the optical absorption spectra of the annealed samples as seen from Fig. 2. In Fig. 3a), the PL spectrum from these samples is shown. The excitation wavelength was 250 nm. A decrease in the PL intensity from the defect state emission bands at 289 nm in the samples annealed under argon is evident. This means that thermal annealing under that atmosphere has not completely passivated the defect states in the silica matrix. On the other hand, the sample annealed under RA shows that the emission band at 289 nm is completely eliminated. However, even though the emission from defects states have been significantly quenched as a consequence of the thermal annealing, it is possible to observe new broader luminescent emission bands emerging in the spectrum at a wavelength range of 400 and 700 nm. NBOHC and POR defects exhibit emission bands within this spectral range as shown in Fig. 1. Nevertheless, it has been observed that the concentration of this defects is significantly

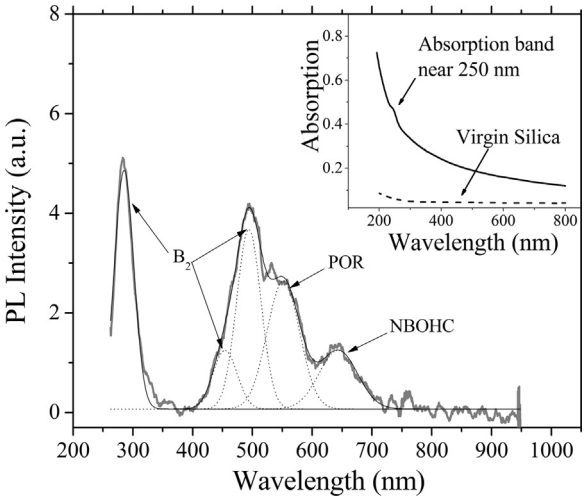

Fig. 1. Photoluminescent from defects state in a silica matrix implanted with Pt ions at 2 MeV. Excitation wavelength was 250 nm. The inset graph shows the optical absorption spectrum of the as-implanted sample. Optical absorption of a virgin silica piece is also shown for comparison.

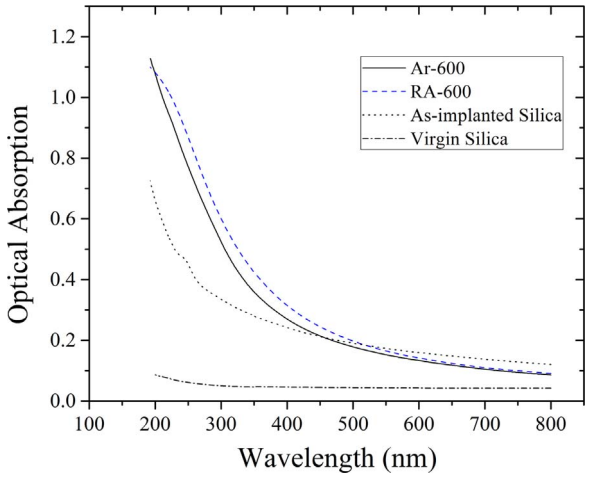

Fig. 2. Optical absorption spectrum of silica implanted with Pt ions at 2 MeV and annealed under two different atmospheres: RA (dashed blue curve) and argon (continued black curve) at 600 °C. The optical absorption spectra of a piece of virgin silica and as-implanted sample is also shown for comparison. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)