9th Int. Symp. "Nanostructures: Physics and Technology"
St Petersburg, Russia, June 18–22, 2001

Scanning tunneling spectroscopy study of three-dimensional nanoscale silicon and platinum assemblies in an opal matrix

C. Díaz-Guerra†, V. G. Golubev‡, *D. A. Kurdyukov*‡, A. B. Pevtsov‡,
J. Piqueras† and M. V. Zamoryanskaya‡
† Departamento de Fisica de Materiales, Facultad de Fisicas,
Universidad Complutense, E-28040 Madrid, Spain
‡ Ioffe Physico-Technical Institute, St Petersburg, Russia

Abstract. Regular systems of Si and Pt nanoclusters have been fabricated in a void sublattice of artificial opal. To incorporate Si into opal voids the thermal CVD technique is used. The samples are filled with Pt from a solution of $PtCl_4$ in ethanol to fabricate metal contacts to silicon. STM and STS are used to investigate the local electronic behavior of Pt-Si nanostructures. It is shown that Si and Pt are regularly distributed inside the opal voids and form nanoscale metal-semiconductor-metal junctions.

Introduction

Synthetic opals, which are composed of ordered amorphous SiO_2 spheres, have attracted interest in the past years because of potential applications of these systems in optoelectronics. Some applications relate to the photonic band gap phenomenon [1]. On the other hand, synthetic opal has a regular sublattice of submicron channels and voids permitting us to obtain three-dimensional (3D) assemblies of Si nanostructures in opal matrices which can be used as the basis of objects for microelectronics, e.g., solid state devices with p-n junctions or Schottky diodes. For the fabrication of opal-based Si solid-state electronic devices it is necessary to deposit a homogeneous layer on the internal surface of the voids and to create metallic contacts. Feoktistov et al [2] have formed Pt-Si contacts by coating the silica spheres with a Pt layer before embedding in Si and demonstrated the possibility of creating 3D multilayer semiconductor structures (p-n junctions or Schottky barriers) on the inner surface of the opal voids. These authors [2, 3] obtained 3D cluster systems with cluster sizes ranging from 1 to 100 nm and a density of elements as high as 10^{14} cm^{-3}. In the present work we use scanning tunneling microscopy (STM) and a spatially resolved scanning tunneling spectroscopy (STS) technique, namely current imaging tunneling spectroscopy (CITS) [4], to investigate the local electronic properties of the opal-Pt-Si samples used in Refs. [2, 3].

1. Experimental details

The opals used in this work consist of SiO_2 spheres of about 250-nm-diameter forming a fcc lattice. The sizes of the octahedral and tetrahedral voids in this lattice are of about 100 and 50 nm, respectively. For the preparation of the opal-Pt-Si samples, the opals were embedded first with Pt and then with Si following the procedure described in Ref. [2]. The fill factors of Si and Pt evaluated from electron probe microanalysis results were 65% and 25%, respectively. Transmission electron microscopy (TEM) has shown [2] that on the surface of the silica spheres different distributions of Pt may result. In some cases,

Pt particles in the range of several nanometers and in different stages of coalescence are observed, while it is also possible to obtain a uniform Pt layer of 5–6 nm thickness. In the samples used in this work the spheres have a discontinuous Pt distribution on their surface.

The samples were observed in the secondary electron mode of a Leica 440 scanning electron microscope (SEM). The STM used was a small size instrument fixed in the chamber of the SEM. The main features of this instrument are similar to the one previously described in [5]. The STM was operated in the constant-current and CITS modes using electrochemically etched or mechanically sharpened Pt-Ir wires as probe tips. CITS provides real space imaging of surface electronic states by recording I–V curves at fixed tip-sample separation at every pixel within an image. In addition to the I–V curves, current images can be formed by plotting the measured current at any voltage. Details of the CITS procedure used here have been described elsewhere [6]. In order to analyze the I–V data of the different points of an image, the normalized differential conductance $(\mathrm{d}I/\mathrm{d}V)/(I/V)$ spectra were used. This quantity removes most of the exponential dependence of tunneling current on tip-sample separation [7] and is proportional to the surface density of states [8, 9].

2. Results and discussion

Figure 1(a) is the STM image, obtained under an applied bias of 0.9 V and 0.3 nA tunneling current, of the contact region of three spheres. The $(\mathrm{d}I/\mathrm{d}V)/(I/V)$ curves recorded on the free surface of the spheres, like the region marked as 1 in Fig. 1(a), show a conduction behavior that depends on the point considered (Fig. 1(b), curves 1, 2). Two different kinds of curves are obtained; one represents a metallic conduction [curve (1)] and is related to the existence of Pt clusters. The other one, in which a surface band gap of about 1 eV is observed, indicates the presence of Si [curve (2)]. In the contact region of the spheres (labeled as 2 in Fig. 1(a)) a more complex behavior has been observed. In addition to the curves attributed to Pt and Si, other curves reveal the existence of surface band gaps in the range 0.5–0.8 eV. An example of this behavior is shown in Fig. 1(b), curve 3. We tentatively explain this result by considering the different species detected in these regions by TEM [2], where the experimentally measured interplanar distances on high-resolution images demonstrated the presence of Pt and Si, but interplanar distances which could not be related to these elements were measured as well. By comparison of the unidentified interplanar distances with those of Pt-Si compounds, close matchings were observed with the $Pt_{12}Si_5$ tetragonal phase and the PtSi hexagonal phase. The formation of the $Pt_{12}Si_5$ phase can take place during the thermal treatment of filled opal fabrication at temperatures at which this phase is formed from Pt deposited on Si wafers [10]. The band gaps in the range 0.5–0.8 eV, measured by tunneling spectroscopy in the area of contact between spheres, could be related to the presence of Pt silicides. This suggestion is also supported by theoretical calculations on the electronic structure of silicides, in which band gaps narrower than that corresponding to Si were predicted [11].

Another specific feature of the conductance measurements performed in these regions is the appearance in some of the curves ($\sim$ 20% of the total analyzed) of negative differential conductance around +2.2 V applied bias voltage (Fig. 2(a)). This effect has been previously reported in tunneling spectroscopy investigations of ultrathin oxide films on Si [12].

The differences in the electronic properties of different regions of the sample, revealed in the $(\mathrm{d}I/\mathrm{d}V)/(I/V)$ curves, are also appreciated in the CITS images. Figure 2(b) shows a CITS image of an opal sample in which an enhanced contrast at the periphery of the spheres, related to local conductance variations, can be clearly observed. In those areas like that marked as 3 in Fig. 1(a) the differential conductance curves show frequently the

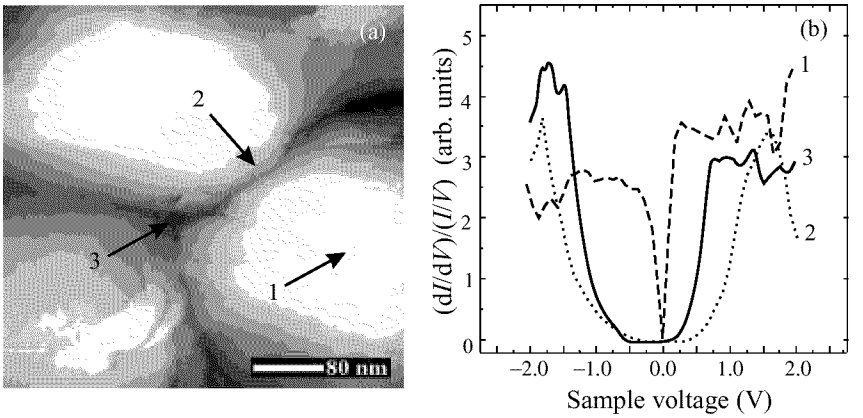

Fig. 1. (a) Constant current STM image showing the contact region of three spheres of an opal. (b) The $(\mathrm{d}I/\mathrm{d}V)/(I/V)$ spectra recorded at regions marked in Fig. 1(a). Curves 1 and 2 are usually obtained at regions marked as 1 in the image. Curve 3 is usually recorded at regions labeled 2 in the figure. Spectra obtained at regions labeled as 3 are similar to curve 1.

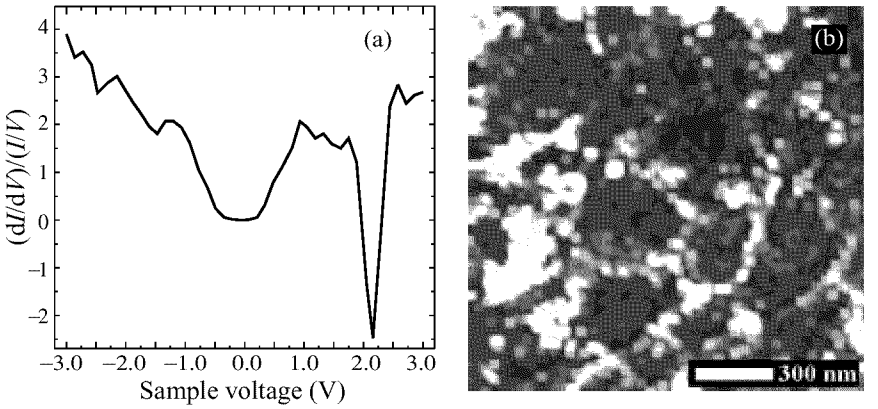

Fig. 2. (a) The $(\mathrm{d}I/\mathrm{d}V)/(I/V)$ curve, showing negative differential conductance at about +2.2 V sample voltage, recorded at the contact region of two spheres of a sample. (b) CITS image acquired at −1.75 V sample voltage in one of the opals. Gray scale range is 2.9 nA.

same metallic behavior shown in Fig. 1(b) (curve 1). This result agrees with the presence of bigger Pt particles observed by TEM in these regions.

3. Conclusions

A 3D regular lattice of Pt-Si nanostructures fabricated using an opal matrix has been characterized by STS. The conductance behavior of the structure has been analyzed with high spatial resolution to determine the presence of Pt and Si in the different regions of the sample. Using STM and spatially resolved STS technique the local electronic properties of opal-Pt-Si composites have been investigated. CITS measurements allowed us to study the I–V behavior and the band gaps in different places of the structure and to observe nanoscale active semiconductor elements.

Acknowledgements

This work was supported by DGES (Project No. PB96-0639) and the Russian R&D program "Nanostructures" (Grant No. 97-2016).

References

[1] Photonic Band Gap Materials, ed. by C. M. Soukoulis. Advanced Studies Institute of NATO, Ser. E, vol. 315 (Kluwer, Dordrecht, 1996).
[2] N. A. Feoktistov, V. G. Golubev, J. L. Hutchison, D. A. Kurdyukov, A. B. Pevtsov, R. Schwarz, J. Sloan and L. M. Sorokin, *Abstr. Mater. Res. Soc. Spring Meeting*, A24.4.1 (2000).
[3] V. N. Bogomolov, N. A. Feoktistov, V. G. Golubev, J. L. Hutchison, D. A. Kurdyukov, A. B. Pevtsov, R. Schwarz, J. Sloan and L. M. Sorokin, *J. Non-Cryst. Solids* **266-269**, 1021 (2000).
[4] R. J. Hamers, R. M. Tromp and J. E. Demuth, *Phys. Rev. Lett.* **56**, 1972 (1986).
[5] A. Asenjo, A. Buendía, J. M. Gómez-Rodríguez and A. Baró , *J.Vac.Sci. Technol. B* **12**, 1658 (1994).
[6] G. Panin, C. Díaz-Guerra and J. Piqueras, *Appl. Phys. Lett.* **72**, 2129 (1998).
[7] J. A. Stroscio, R. M. Feenstra and A. P. Fein, *Phys. Rev. Lett.* **57**, 2579 (1986).
[8] N. D. Lang, *Phys. Rev. B* **34**, 5947 (1986).
[9] R. M. Feenstra, J. A. Stroscio and A. P. Fein, *Surf. Sci.* **181**, 295 (1987).
[10] B. Tsui and M. Chen, *J. Appl. Phys.* **68**, 6246 (1990).
[11] O. Bisi and C. Calandra, *J. Phys. C* **14**, 5479 (1981).
[12] H. Watanabe, K. Fujita and M. Ichikawa, *Appl. Phys. Lett.* **72**, 1987 (1998).