

Communications

Growth of Tin Oxide in Opal**

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Since opal consists of an ordered face-centered cubic (fcc) array of SiO_2 balls,^[1] which leads to a regular periodic modulation of the dielectric constant between that of the SiO_2 balls ($\epsilon = 2.1$) and that of the voids ($\epsilon_{\text{air}} = 1$), it is a photonic bandgap (PBG) material. As the size of the opal spheres is in the submicrometer range, the effect is seen using the Bragg diffraction of visible light. If the voids are infilled with a material of much higher dielectric constant, the modulation, and hence the intensity of the PBG effect, is increased. There is some interest in the enhancement of these PBG materials as, at strong modulation, a transparent material becomes opaque at certain frequencies, which could lead to the inhibition of spontaneous emission and hence the improved efficiency of lasers.^[2]

We have previously demonstrated the increase in PBG behavior (as determined by Bragg reflection) upon infilling the voids with either InP ^[3] ($\epsilon = 12.3$) or GaP ^[4] ($\epsilon = 10.9$). These materials have much larger dielectric constants than SiO_2 (and the air in the voids). The dielectric constant of tin oxide ($\epsilon = 2.9$) is much lower than that of InP and GaP , though still larger than that of SiO_2 . This still leads to an increased refractive index contrast between the opal spheres and their voids, again showing an enhancement of PBG behavior. However, the main reason for the addition of tin oxide relates to the possibility of achieving electrical contacts throughout the infilled opal, rather than just on the outer surface. When suitably doped, tin oxide is a good conductor. A conducting surface throughout the opal sample should increase the ease of electrical contact to the infilled opal. Synthetic opals were infilled with tin oxide to ca. 33 % void volume by CVD. The method of deposition, either by alternate addition of the reactants or as standard layer growth in which the reactants are added at the same

time, gives different results. In this preliminary communication we look at the ease with which tin oxide may be grown in opal structures using CVD.

As could be seen by X-ray diffraction (XRD), both growth methods produced tin oxide. Figure 1 shows the XRD spectrum for the cyclically grown sample, which was

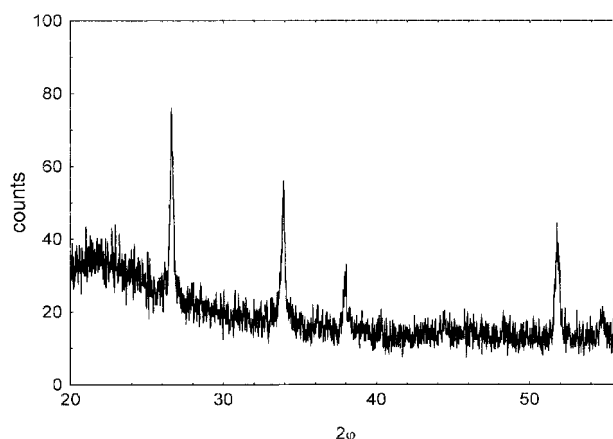


Fig. 1. XRD spectrum of opal infilled with tin oxide by the cyclic growth method. The bars represent the positions of peaks for tin(IV) oxide from the JCPDS database.

of lower intensity than that of the sample in which the reactants were added together, although the two spectra had the same diffraction peaks. This was fitted from the JCPDS database to tin(IV) oxide (03-1114).

Looking first at the sample in which the reactants were added together, this sample showed no shift in the Bragg reflectance from the bare opal. This implies that the tin oxide was a mainly surface coating. The scanning electron microscopy (SEM) images (sphere size 300 nm) shown in Figure 2a confirmed that growth was mainly on the surface, the external tin oxide layer thickness being about 1 μm . However, a depth profile of the tin concentration (Fig. 2b) did show a very small infill to about 3 μm , the tin signal dropping off rapidly at a depth of 10 μm .

Looking next at the cyclically grown sample, the Bragg reflectance shows a large shift from that of the bare opal, confirming that the infill is within the opal and not just on the external surface. In Figure 3a, a series of reflectance measurements at various incident radiation angles are shown. The extent of change in the stop-band position can be clearly seen in Figure 3b, which shows a plot of the wavelength of the stop-band against a function of the angle of incidence radiation for both the bare and infilled opal. This shows a shift of approximately 80 nm, which corresponds to a 33 % pore volume infill. This was calculated using a similar method to that used to calculate InP infill.^[4]

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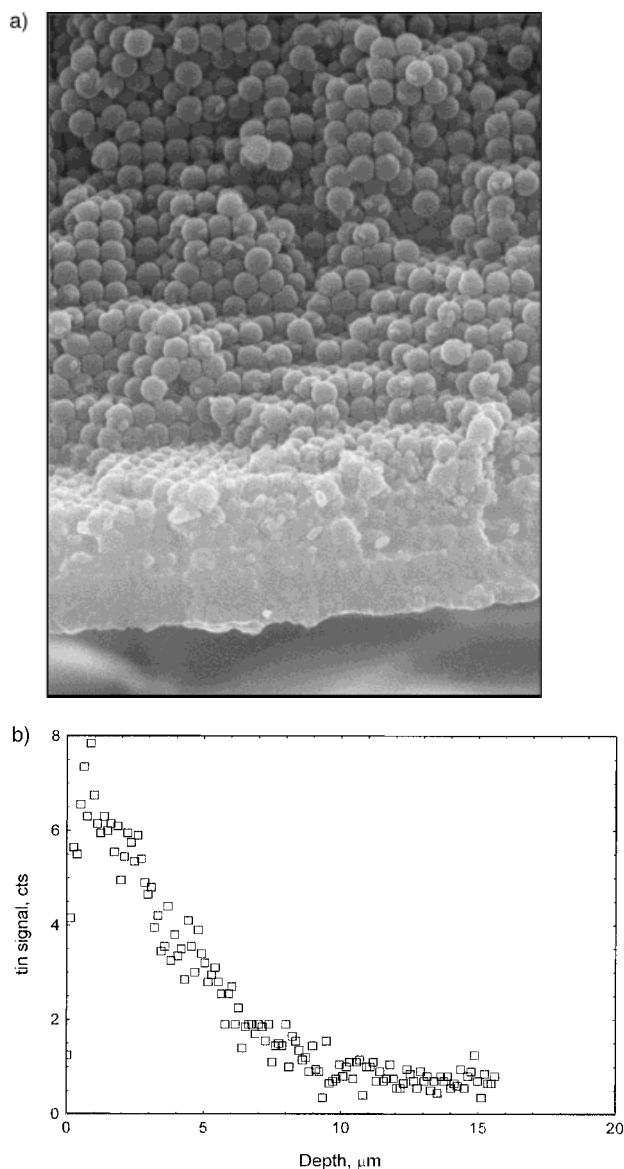


Fig. 2. Result of reactants being added together. a) SEM image (opal sphere size 300 nm). b) Depth profile.

SEM images of the cyclic growth (Fig. 4a) establish that the tin oxide coats the opal spheres (465 nm) as a shell, in a manner similar to that of GaP.^[5] Calculations from both Bragg diffraction and SEM show that the opal spheres are coated with tin oxide to a thickness of about 18 nm. A preliminary depth profile (Fig. 4b) shows a relatively even infill throughout the sample thickness of 400 μm. However, this technique does not allow for the existence of voids between the opal spheres and assumes full infill, so the values produced for the tin levels are only qualitative. This means that it is not possible to compare the absolute amounts of infill for the two samples.

The uniformity of the tin oxide coating produced via cyclic growth is of interest since continuous films are desirable in order to be able to inject electrons into the opal structures. Such an approach may permit electron or hole trans-

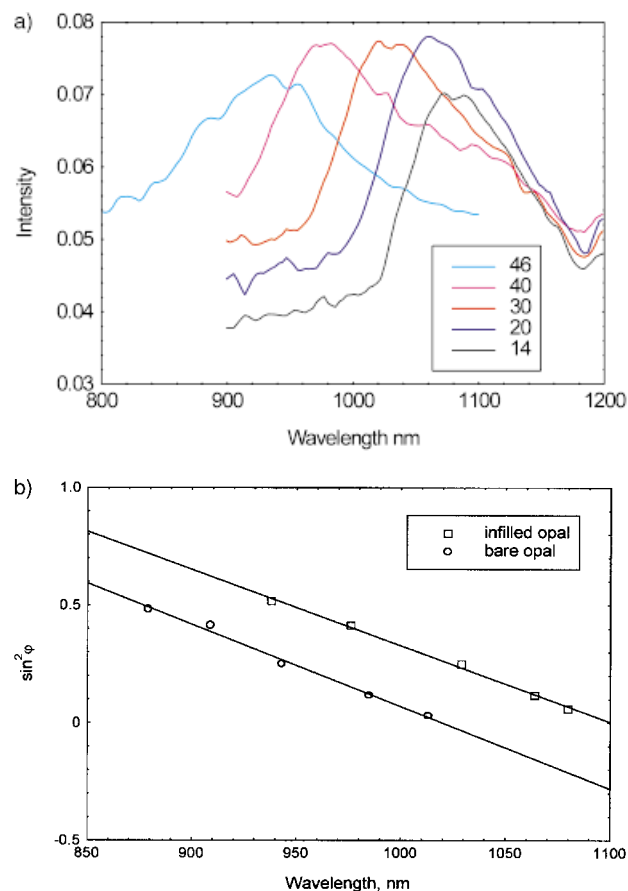


Fig. 3. a) Bragg diffraction of the infilled opal at various angles of incident radiation. b) Graph showing the shift in the stop-bands between bare and infilled opals.

port through other materials, such as optoelectronically active semiconductors or electroactive dye systems, grown within the opal structures. Clearly, if appropriate structures can be grown and electrical contact established using tin oxide film, this raises the possibility of housing a light-emission source within the structure itself. It is suggested here that this approach may lead to the production of an entirely new class of optoelectronic photonic bandgap structures and devices, including light-emitting diodes, lasers, and waveguides.

In conclusion, this work confirms our general observation that cyclic growth, rather than simultaneous addition of the reactants, is necessary in order to obtain infilled opal rather than surface growth. For cyclic growth, success has already been achieved, with high tin oxide infill values of 33 % pore volume, giving rise to a large shift in the stop-band as shown by Bragg reflectance. The infill was shown to be polycrystalline, coating the opal spheres as a shell to a thickness of about 18 nm. It was also shown that the tin oxide is homogeneously deposited within the opal structure. More work will be needed to optimize this tin oxide infill procedure, and then dope the infill to produce conducting material for electrical contacts.

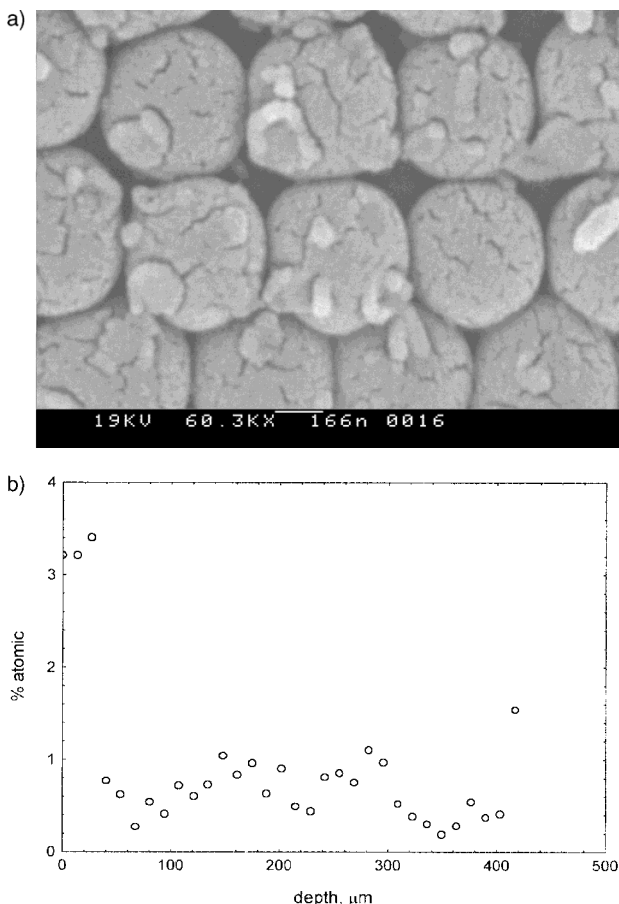


Fig. 4. Result of cyclic addition of reactants. a) SEM image (coated opal sphere size 482 nm). b) Depth profile.

Experimental

The opal samples used, synthesized by a method previously reported [5], had sphere diameters of 300 nm and 465 nm. A CVD tin oxide coater, as described in the literature [6], was used with reactants of dimethyl-dichloro tin (DMT) and water vapor. However, unlike the previous method, no additional oxygen was added. To keep the growth rate low, reactant concentrations were as small as could be accurately determined on this coater (approximately 6×10^{-4} mol min $^{-1}$ of DMT and water vapor). The DMT bubbler was held at 110 °C, and the water at room temperature. All lines were heated to 180 °C to prevent blockages. Two methods were used to infiltrate the opal, both at atmospheric pressure. In the first, the reactants were added together at 645 °C for 12 min (as if for a standard tin oxide coating). The second (as previously carried out by us for semiconductors in opal) consisted of the alternate addition of the reactants for four growth cycles of 10 min each, again at 645 °C.

Both the bare and infiltrated opals were characterized by a variety of methods. The photonic behavior was determined by use of reflectance measurements. Samples were irradiated with plane-parallel white light from tungsten (NIR) and xenon arc (visible) lamps at different angles with respect to the (111) surface normal. Due to the coherent scattering of light from the ordered submicrometer-size spheres in the opal, Bragg reflections are seen. When the opal is infiltrated (with material of higher refractive index than the air displaced in the opal voids) these Bragg reflections are shifted to higher wavelengths. The actual shift is dependent on the amount of infiltrate, which can be calculated as shown in a previous paper [7]. XRD spectra were obtained from a Siemens D5000 powder diffractometer in order to check the crystallinity and type of tin oxide formed, the latter by fitting to standard curves from the JCPDS database.

Tin density profiles were measured on freshly cleaved edges observable (after fracturing the infiltrated samples) by means of SEM (JEOL 6300). In order to do this, we performed energy dispersive X-ray (EDX) spectrometry

(detector LINK EDS, Oxford Instruments, model ISIS-200) at several regularly spaced points along a line from the outer surface to the center of the sample. All results were corrected for topographic effects by comparing the tin signal coming from the sample with the secondary electron scattering.

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High-Conductivity p-Type Transparent Copper Aluminum Oxide Film Prepared by Plasma-Enhanced MOCVD

By Yue Wang and Hao Gong*

Unlike conventional semiconductors such as Si, Ge, and GaAs, transparent semiconductors can allow visible light to pass through whilst absorbing UV light. The availability of transparent semiconductor devices would lead to numerous applications, such as ultraviolet-emitting diodes, and functional windows that not only transmit visible light, but also convert UV light into electric power. Unfortunately, although n-type transparent semiconductors such as ZnO, SnO₂, and indium tin oxide (ITO)^[1–5] are well developed, only very limited p-type transparent semiconductors have been reported, and the conductivity of these is far below that of n-type ones. It is this unequal development that is the main barrier to the successful production of transparent p–n junctions or devices for significant applications.

Up to now, only very limited p-type transparent conducting oxide (TCO) thin films have been fabricated. Most of these films showed either low conductivity, or low transmittance. ZnO doped with N had a conductivity of 10^{–2} S cm^{–1}, and the color was brown.^[6] In₂O₃–Ag₂O had a conductivity of 10–10³ S cm^{–1}, with a low average transmittance of 20 % in the visible range.^[7] The most successful one was the recently reported CuAlO₂ thin film with conductivity 9.5 × 10^{–2} S cm^{–1}, with a transmittance ranging from 27 % to 52 % in the visible range.^[8] Such a conductivity is much higher than that of the other p-type films, but still much lower than that of n-type transparent semiconductors (conductivity 10³ S cm^{–1}, transmittance 80 %).

The thickness of the PE-MOCVD film within the semiconductor industry, the most widely used film deposition tech-

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