Structural state of InSb in InSb/opal composite material according to transmission electron microscopy data

© A.E. Kalmykov, L.M. Sorokin, D.A. Kurdyukov

Ioffe Institute,
194021 St. Petersburg, Russia

E-mail: aekalm@mail.ioffe.ru

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The structural state of indium antimonide introduced into the opal matrix was studied by high-resolution transmission electron microscopy. It is shown that the filler has a microcrystalline structure with grain sizes an order of magnitude larger than the dimensions of individual matrix pores. The defective structure of individual crystals is characterized.

Keywords: composite, opal, InSb, transmission electron microscopy.

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1. Introduction

Composite materials based on synthetic opals continue to attract the attention of researchers [1–4] because of the possibility of using them to control electromagnetic energy flows [5,6].

Synthetic opals, like natural opals, consist of balls of amorphous silica (SiO_2) forming a face-centered cubic lattice [7,8]. The diameters of the balls (D) are in the range of $0.15-1\,\mu$m. The calculation shows that, assuming a point contact of the balls, the proportion of pores between the balls accounts for up to 26% of the total volume. There are two types of pores in the opal: tetrahedral with the size of $0.23D$ and octahedral with the size of $0.41D$, connected by channels with a cross section of $0.155D$ [9] and also forming a three-dimensional periodic structure. The optical contrast index $\eta = (\varepsilon_v/\varepsilon_s)/2$ of the composite thus obtained can be changed by introducing various substances. Here ε_v and ε_s are dielectric constants of filler and balls. When the contrast value of $\eta > 2.8$ is reached, a complete photonic band gap is formed in the composite [10]. The contrast of pure opal is insufficient for this, so it is necessary to introduce a filler with a high refractive index, for example, semiconductor materials. The matrix material is removed by liquid etching to further increase the contrast. The result is a so-called inverted opal structure.

We have not been able to find in the literature any results of a detailed study of the structural state of semiconductor fillers despite the fact that a large number of papers are devoted to the study of the properties of composite materials based on synthetic opals. At the same time, if a semiconductor material is used as a filler, then its electronic and optical properties largely depend on its structural state.

The purpose of this work is to study the structural state of indium antimonide (InSb) as an opal matrix filler.

InSb is a narrow-band direct band semiconductor with a sphalerite structure with a sufficiently high refractive index $n = 4$ in the infrared range [11]. This material is used as infrared photodetectors.

2. Experiment procedure

Synthetic opal was produced using Stöber method [12] in the form of densely packed balls of amorphous silica with a diameter of ~ 230 nm. InSb filled the matrix in a liquid state (melting point 527°C) under the action of capillary forces in a vacuum chamber to prevent reaction with oxygen [13]. The degree of filling was 98 ± 3 vol% according to gravimetric measurements. The density of indium antimonide decreases from 6.5 to 5.77g/cm^3 during crystallization. Given that the thermal expansion coefficient (TEC) of amorphous silica is very small, and the temperature decrease during crystallization is insignificant, it should be expected that the filler will be in a highly stressed state. The composite was kept at the melting point of InSb for 30 minutes so that the excess filler left the matrix. Then the composite was cooled to room temperature. The degree of filling fell by 0.7 vol.% since the InSb TEC is more than 10 times higher than the SiO_2 TEC ($5.4 \cdot 10^{-6}\,K^{-1}$ and $0.5 \cdot 10^{-6}\,K^{-1}$, respectively).

The samples for the TEM study were prepared using standard methods, including slicing and grinding, followed by ion etching with argon ions. As shown by preliminary experiments, the filler remained in the matrix during the thinning process and under the impact of the electron beam of the microscope in the composite samples. Structural studies were performed using a transmission electron microscope JEOL 4000EX(II) with an accelerating voltage of 400 kV. EDX spectra were recorded using a JEOL 2010 microscope with a Si(Li) detector.

3. Experimental results and discussion

TEM images obtained at low magnifications (from 5000x) demonstrated that the filler formed a three-dimensional grid, filling the communicating pores. The analysis of EDX spectra did not reveal any deviation of the composition of the material in the pores from the stoichiometric InSb. Microdifraction patterns (Figure 1, *b*) showed that the filler is in a monocrystalline state in areas of the sample with an area of several square micrometers, i. e. these areas significantly exceed the size of individual pores.

Twin inserts were found in the filler crystals. InSb region with an orientation ⟨111⟩ parallel to the electron beam was selected since the electron diffraction corresponded to the material with a FCC lattice. The microdifraction patterns recorded along the axis of the zone corresponded to a lattice with twins, which are found in TEM images. The twin inserts had the shape of elongated strips with a long side up to 700 nm, which exceeds the size of one pore of the matrix (Figure 1, *a*). The transverse size of the inserts < 30 nm. The geometric structure of the matrix is such that a straight line segment up to $4D\sqrt{3}$ can be drawn through adjacent pores, in our case — 1600 nm [9]. The minimum transverse size of the channels between the voids is 36 nm. Thus, the observed inserts are located immediately in neighboring pores — in two (or one) tetrahedral and one octahedral. The fact that the crystallographic orientation of InSb in the pores and channels is the same indicates the mechanism of directional crystallization during cooling.

Electronic micrographs recorded in high-resolution mode made it possible to characterize the boundaries between the twins. For the most part, these are coherent boundaries that coincide with the plane {111}, which is the plane of twinning of crystals with a cubic face-centered structure. There are also borders consisting of facets with orientation $\{11\bar{1}\}$ and facets perpendicular to them with orientation $\{11\bar{2}\}$. The length of the facets ranges from the size of the InSb lattice cell order (Figure 2, *a*) to 10 nm (Figure 2, *b*).

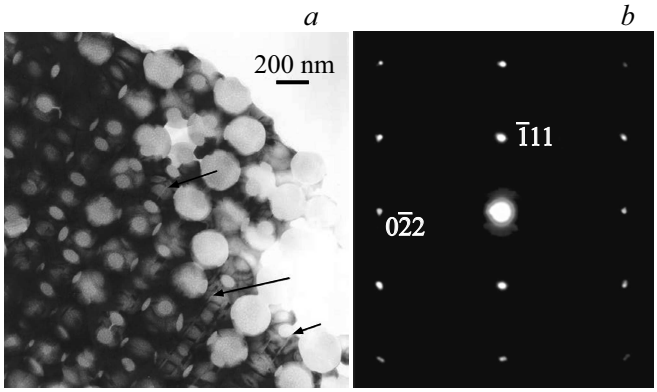

Figure 1. TEM image of the InSb/opal composite (*a*). The arrows indicate twin inserts. The pattern of electronic microdifraction recorded from the composite. Axis of the zone ⟨211⟩ (*b*).

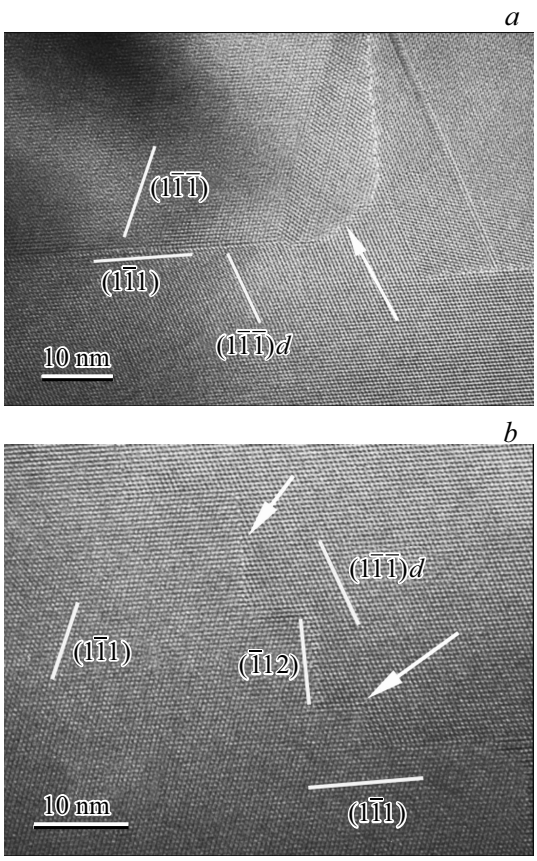

Figure 2. Images of various sections of the composite, recorded in high resolution mode from different sections of the sample. The beam incidence direction [110]. The white lines indicate the positions of the planes {111}. $(1\bar{1}\bar{1})d$ — Miller indices of the twin planes. The arrows indicate the boundaries between the twins.

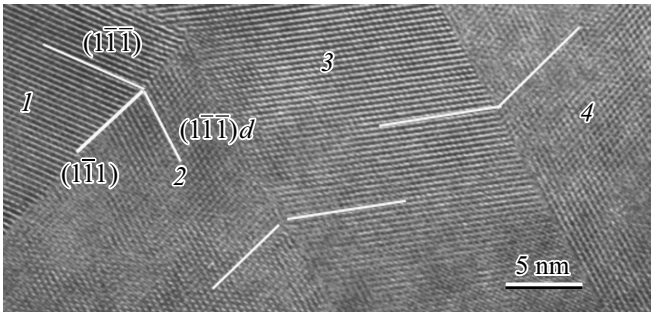

Figure 3. Sequential twinning of InSb. The beam incidence direction [110]. The white lines indicate the positions of the planes {111}. $(1\bar{1}\bar{1})$ — Miller indices of the twin planes.

The phenomenon of sequential twinning with respect to the planes {111} was discovered. Figure 3 shows an example of such a phenomenon. It is clearly seen that the grains *1–4* are the result of sequential twinning.

As mentioned above, the filler turns out to be in a highly compressed state as a result of crystallization, which means that the observed deformation of the filler occurs by the

twinning mechanism. No other significant structural defects were found.

4. Conclusion

Thus, it is shown that the filler material is in a monocrystalline state in significant volumes of the opal matrix, the channels between the pores are also filled with crystalline InSb with the same orientation. The twinning along the planes was the only significant violation of the order $\{111\}$.

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Conflict of interest

The authors declare that they have no conflict of interest.

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