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Evolution of silver in a eutectic-based Bi$_2$O$_3$–Ag metamaterial

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ABSTRACT

The development of novel manufacturing techniques of nano-/micromaterials, especially metallodielectric materials, has enabled dynamic development of such fields as nanoplasmonics. However, the fabrication methods are still mostly based on time-consuming and costly top-down techniques limited to two-dimensional materials. Recently, directional solidification has been proposed and utilized for manufacturing of volumetric nanoplasmonic materials using the example of a Bi$_2$O$_3$–Ag eutectic-based nanocomposite. Here, we explain the evolution of silver in this composite, from the crystal growth through the post-growth annealing processes. Investigation with tunneling electron microscopy shows that silver initially enters the composite as an amorphous AgBiO$_3$ phase, which is formed as a wetting layer between the grains of Bi$_2$O$_3$ primary phase. The post-growth annealing leads to decomposition of the amorphous phase into Bi$_2$O$_3$ nanocrystals and intergranular Ag nanoparticles, providing the tunable localized surface plasmon resonance at yellow light wavelengths.

Introduction

Plasmonics [1, 2] is currently one of the rapidly developing fields due to its role in enhancing optical properties, which makes it useful for application in solar cell efficiency enhancement [3, 4], cancer treatment [5], improved hard disks [6], lasers [7] and home-used diagnostics [8]. To achieve plasmonic effects on local field enhancement, localized surface plasmon resonance (LSPR) or surface plasmon propagation, an interface between two media—plasmonic (metallic-like) and dielectric—is needed [9]. Due to the collective oscillations of free charges, which are responsible for negative real permittivity, metals like silver and gold are currently the most used materials in plasmonics [10]. However, though other plasmonic materials have been considered [11, 12], it is still silver in the visible wavelengths, which is most widely used due to its lowest optical losses [13] and highest electrical conductivity at room temperature [14].
Recently, eutectic solidification [15, 16] has been proposed as one of the most promising bottom-up methods for manufacturing of metamaterials [17–20], plasmonic materials [21, 22] and photonic crystals [23, 24]. Eutectic solidification enables crystallization of a two-phase solid, often with an interesting self-organized micro-/nanostructure (typical are rod-like and lamellar structures) from a miscible liquid phase at a certain temperature [25]. Eutectic composites have been investigated for various applications such as solar energy conversion [26–28], power generation gas turbines [29], scintillators [30, 31] or second-harmonic generators [32]. The plasmonic effect was presented in a eutectic composite for the first time with a Bi$_2$O$_3$–Ag composite [21, 22]. After annealing the Bi$_2$O$_3$–Ag eutectic material, metal nanoparticles (silver and bismuth) are formed, which are responsible for the occurrence of plasmonic resonance in the visible wavelength range, at ~595 nm. Using different annealing conditions such as the atmosphere, time and temperature, it is possible to control the peak frequency of the LSPR [22]. However, the development of metallic silver in this material is not yet well understood. Here, we demonstrate the evolution of silver in a Bi$_2$O$_3$–Ag eutectic starting from the crystal growth, and formation of the microstructure, through the influence of the post-growth annealing of the samples on its micro-/nanostructure and thus the optical properties. The analysis is based on high-resolution transmission electron microscopy (HRTEM) and selected area diffraction (SAD).

Materials and methods

The Bi$_2$O$_3$–Ag material was obtained by the micro-pulling down method [33, 34] in a nitrogen atmosphere from pure powders of bismuth oxide (Alfa Aesar, 99.99% purity) and silver (Alfa Aesar, 99.95% purity). Detailed growth and preparation methods have been described elsewhere [21]. After growth, the samples were annealed in vacuum at 600 °C for 60 min [22]. The obtained Bi$_2$O$_3$–Ag composites were characterized by the following methods: high-resolution transmission electron microscopy (HRTEM) connected with selected area electron diffraction and with scanning transmission electron microscopy (STEM) with energy-dispersive X-ray spectroscopy (EDX). Samples for transmission electron microscope analysis were prepared by a focused ion beam (FIB) lift-out technique using a 30-keV Ga+ ion beam in an AURIGA CrossBeam Workstation (Carl Zeiss) equipped with a Canion FIB column (Orsay Physics). TEM investigations were conducted with the use of a Tecnai F20ST (FEI) TEM-STEM microscope with field emission gun and electron beam energy of 200 keV and coupled to a high-angle annular detector (HAADF) and a EDAX X-ray energy-dispersive spectrometer (EDX). The software “TE Imaging & Analysis” (EI) was used to provide standardless semiquantitative analyses of the EDX spectra. These analyses take into account the thickness and the chemical elements of the thin foil (ZAF corrections) and use preregistered K factors. Differential scanning calorimetry/thermogravimetry (DSC/TG) measurements were taken on an STA 449 (NETZSCH) with a platinum furnace under argon flow with different amounts of purge oxygen. Stoichiometric portions of powders were measured out and mixed manually with minor addition of isopropyl alcohol until a homogeneous color was achieved. The mixture was subsequently dried at 80 °C to remove the alcohol. The signals were measured with a Pt–Rh thermocouple using platinum crucibles in a temperature range from room temperature to 1173 K with a heating/cooling rate of 10 K min$^{-1}$. Bi$_2$O$_3$–Ag powder mixtures were heated to 1173 K and cooled to 923 K. The process was repeated three times in each atmosphere to ensure homogeneity of the melt. The solidus temperatures were extracted from the heating curves as onset values, whereas liquidus temperatures were extracted from the cooling curves as the end temperatures. The influence of oxygen content on the phase diagram was investigated using powder samples of mixed bismuth oxide (99.99% purity) with silver (99.95% purity) in the range of 0–10 mol% in steps of 1 mol%.

Results and discussion

From the Ag-$\frac{1}{2}$(Bi$_2$O$_3$) phase diagram [35] in the mentioned system, several transformations at an oxygen partial pressure of 1.01 × 10$^5$ Pa are observed (1) allotropic of Bi$_2$O$_3$, $\alpha$-Bi$_2$O$_3$ → $\delta$-Bi$_2$O$_3$), (2) monotectic (Ag) + Liq2 ↔ Liq1 at 939 °C and eutectic reaction (Ag) + $\alpha$-Bi$_2$O$_3$ ↔ Liq2 at 687 °C with a composition of 18.54 mol% Ag and 81.46 mol% Bi$_2$O$_3$ ($\sim$8.6 vol% Ag). With the decrease in oxygen content in the atmosphere, the composition of the
eutectic point shifts toward lower content of silver (12.3 mol% Ag for $pO_2 = 2.1 \times 10^4$ Pa, $\sim 5.5$ vol% Ag). In our growth experiments, the successful composition that led to good-quality Bi$_2$O$_3$–Ag rods was 15.4 mol% Ag and 84.5 mol% $\frac{1}{2}$Bi$_2$O$_3$ ($\sim 7.8$ vol% Ag). This composition is between the eutectic points determined by Assal et al. [35] for different oxygen partial pressures, as shown in Fig. 1. We have confirmed part of the phase diagrams investigated by Assal et al. with DSC/TG measurements for different partial pressures of oxygen: $pO_2 = 0.32 \times 10^4$, $0.77 \times 10^4$, $1.43 \times 10^4$ and $2 \times 10^4$ Pa. It can be noticed that the liquidus line is in a very good agreement; however, the solidus line yielded a slightly lower temperature.

The as-grown Bi$_2$O$_3$–Ag composite is characterized by a three-dimensional micro-/nanostructure of silver-containing phase in a Bi$_2$O$_3$ matrix. Silver is located in a second phase wetting the Bi$_2$O$_3$ grain boundaries and at triple points where it adopts a triangular shape. Between two Bi$_2$O$_3$ grains, silver is in the form of plates with lengths of several tens of microns and thicknesses of a few nanometers.

To investigate the phase in which silver is placed in the Bi$_2$O$_3$–Ag composite during growth and to understand the processes which lead to the formation of silver nanoparticles after the annealing of the material, high-resolution transmission electron microscopy has been performed on the as-grown and annealed-in-vacuum samples. Both the selected area electron diffraction and the energy-dispersive X-ray spectroscopy confirmed that the as-grown material consists of two phases. In the region analyzed, the dominant phase is $\gamma$-Bi$_2$O$_3$ (bcc, $a = 1.027$ nm), which was detected in the larger grains. These grains enclosed smaller grains, which were probably the $\alpha$-Bi$_2$O$_3$ phase. However, the second phase previously not recognized by other techniques is an amorphous (halo in the SAD pattern) phase containing Bi, Ag and O, with an atomic ratio Bi/Ag $\approx 1$, as shown in Fig. 2. The shape of this second phase, forming triangles at Bi$_2$O$_3$ triple points and wetting the Bi$_2$O$_3$ grain boundaries, is consistent with the solidification of a liquid after the crystallization of the major primary phase, in this case Bi$_2$O$_3$. The radius of the halo in Fig. 2e provides the distance of the first neighbors in the amorphous phase, which is 0.32 nm (superimposed with the $d_{310} = 0.325$ nm of $\gamma$-Bi$_2$O$_3$). This distance does not match with the strongest reflections of silver or silver oxides but with the strongest reflections of $\gamma$-Bi$_2$O$_3$ as well as with those of an ilmenite-type, AgBiO$_3$ phase [36]. The amorphous phase might enclose clusters of atoms prefiguring an ilmenite crystal. Ilmenite-type oxides have two kinds of combinations of metal cations: $A^2+M^{4+}$O$_3$ and $A^3+M^{5+}$O$_3$ [37], where AgBiO$_3$ corresponds to the second one.

Due to a strong dependence of the eutectic point on the content of oxygen in the atmosphere, it is not
clear whether the composition of the Bi$_2$O$_3$–Ag composite we have grown is shifted to a higher abundance of Bi$_2$O$_3$ or Ag, as shown in Fig. 1. From the phase diagram of Bi$_2$O$_3$–Ag [35], if the composition is shifted from the eutectic point to a higher abundance of Bi$_2$O$_3$, it is the Bi$_2$O$_3$ phase that should crystallize first in contact with a liquid phase. While, if the composition is shifted toward a higher abundance of Ag, the Ag phase should crystallize first, and then, the eutectic will be made of Bi$_2$O$_3$ and Ag.

The geometry of the Ag–Bi–O phase placed in between the grains of Bi$_2$O$_3$ is typical of a liquid phase that solidified after the main grains, though potentially it could be a Ag-containing phase in which the grains were squeezed by growing Bi$_2$O$_3$ grains. The AgBiO$_3$ phase is probably formed in the following reactions [38]: 4AgO + Bi$_2$O$_3$ → 2AgBiO$_3$ + Ag$_2$O, and Ag$_2$O + Bi$_2$O$_3$ → 2AgBiO$_2$.

The amorphous Ag–Bi–O phase is not stable when irradiated by the electron beam and partially

Figure 2 Structural analysis of the as-grown Bi$_2$O$_3$–Ag eutectic material. a Bright-field image of the entire FIB cut of the sample with selected phases. b, c STEM-HAADF images of chains of Bi$_2$O$_3$ nanocrystals within the γ-Bi$_2$O$_3$ matrix, potentially also γ-Bi$_2$O$_3$. The γ-Bi$_2$O$_3$ larger grain encloses chains of smaller α-Bi$_2$O$_3$ grains. d STEM-HAADF image and e SAD pattern across Bi$_2$O$_3$- and Ag-based phase. Spots corresponding to the γ-Bi$_2$O$_3$ are in [001] zone axis. The halo is formed by the second phase and is typical of an amorphous phase. f Chain of probable α-Bi$_2$O$_3$ grains within bigger grains of γ-Bi$_2$O$_3$. EDX spectrum of g the AgBiO$_3$ phase, h γ-Bi$_2$O$_3$ matrix and i Bi$_2$O$_3$ larger grains.
decomposes into ca. 50-nm-diameter $\gamma$-Bi$_2$O$_3$ nanocrystallites and metallic silver particles a few nanometers in size. Nanocrystals of bismuth oxide up to 50 nm in size are clearly seen in the dark-field image (Fig. 3a) and as bright spots at the SAD image (Fig. 3b). The first internal ring is from the amorphous Ag–Bi–O phase. A second finer halo at 0.23 nm is clearly observed, which may correspond to metallic nanosilver (strongest reflection 111 Ag fcc) exsolved from the Ag–Bi–O phase, with sizes of a few nm, as shown in Fig. 3b.

Concerning the optical properties of the Bi$_2$O$_3$–Ag composite, it has been previously confirmed that only the annealed samples demonstrate LSPR, due to the formation of Ag nanoparticles after the post-growth annealing [21]. The best of the investigated annealing conditions, which led to the most intensive LSPR peak, was annealing at 600 °C for 60 min in vacuum [22]. That is why such samples were investigated here further, as shown in Fig. 4. In the vacuum-annealed samples in comparison with the as-grown (un-annealed) samples, it can be seen that the large Bi$_2$O$_3$ grains did not change, while the amorphous phase transformed during the annealing into $\gamma$-Bi$_2$O$_3$ grains several hundreds of nm in size, as shown in Fig. 4a–c, and intergranular precipitates of Ag a few nm in size (Fig. 4d, red circle), as confirmed by EDX.

Both the annealing and irradiation with the electron beam during the TEM experiments resulted in phase and structural change of the material, which can be the result of a few processes. Thermal stability studies of AgBiO$_3$ [39] performed in argon show weight loss from AgBiO$_3$, which corresponds to two transitions such as:

$$\text{AgBiO}_3 \xrightarrow{250–280^\circ C} \text{AgBiO}_2 \xrightarrow{300–550^\circ C} \text{Ag} + \text{Bi}$$

As a result of the final decomposition of AgBiO$_3$, a mixture of metallic silver and bismuth can be obtained. The formation of both Ag and Bi nanoparticles was already previously observed by us in this material [22]. This suggests that it is the decomposition of AgBiO$_3$ into Ag and Bi nanoparticles in between the big Bi$_2$O$_3$ grains, which probably causes the formation of the smaller (ca. few hundred nanometers in size) Bi$_2$O$_3$ grains. The few-hundred-nm-in-size Bi$_2$O$_3$ grains have grown from the nano-Bi$_2$O$_3$ grains seen in Fig. 3a, with decomposition of the amorphous phase. In Fig. 5, we illustrate the proposed mechanism of silver evolution in the Bi$_2$O$_3$–Ag system.

**Conclusions**

In summary, an explanation of the evolution of silver in a Bi$_2$O$_3$–Ag eutectic composite from the crystal growth through the post-growth annealing processes has been presented. In the as-grown samples, silver is inserted in an amorphous phase enclosing AgBiO$_3$ clusters, which is formed as intergranular films and triple points wetting the grains of Bi$_2$O$_3$ primary phase. After the post-growth annealing, the AgBiO$_3$ phase decomposes into Bi$_2$O$_3$ nanocrystals and intergranular Ag. These studies give us an explanation for the origin of silver nanoparticles in the Bi$_2$O$_3$–Ag eutectic-based material after the annealing procedure and thus the localized surface plasmon resonance at yellow light wavelengths.

![Figure 3](https://example.com/figure3.png)  
*Figure 3* Decomposition of the amorphous AgBiO$_3$ phase under electron beam irradiation into nanocrystalline $\gamma$-Bi$_2$O$_3$ precipitates and metallic silver to $\gamma$-Bi$_2$O$_3$ seen as bright grains in the dark-field image and as spots in the indexed SAD. SAD showing the formation of Ag–Bi–O amorphous phase (first smaller ring at 0.32 nm) and nanocrystals of silver (second finer ring at 0.23 nm).
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Figure 4 Structural analysis of the annealed-in-vacuum Bi$_2$O$_3$–Ag eutectic material. a–c Progressive zooms by HAADF showing the various scales of the structure with the smaller and larger grains marked, d, e intergranular precipitates of Ag presented by HAADF with EDX analysis.

Figure 5 Silver evolution mechanism in Bi$_2$O$_3$–Ag system, starting from the crystal growth through the post-growth annealing processes. Blue arrows represent processes, red rectangles—the resulting micro-/nanostructure. SEM pictures of the microstructures a before and c after annealing. STEM-HAADF image b across Bi$_2$O$_3$- and Ag-based phase and d intergranular precipitates of Ag.

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