Synthesis of Plasmonic Nanoparticles for Hybrid Nanophotonic Materials

Yugang Sun and Gary Wiederrecht
Nanophotonics Group, Center for Nanoscale Materials, Argonne National Laboratory
9700 South Cass Avenue, Argonne, Illinois 60439

Scientific Thrust Area

The scientific thrust area of the research is to develop new routes to functional nanophotonic materials. In this thrust, we pursue the development of new optical materials via advanced colloidal synthesis to generate hybrid nanoscale structures over large areas.

Research Achievement

One of the most important successes is the direct growth of anisotropic metal nanoplates with clean surfaces on semiconductor substrates. In general, metal nanoparticles with varying shapes are synthesized through the well-developed solution-based approaches, which rely on surfactant molecules to direct the anisotropic growth of metal nanoparticles, followed by deposition of them on the desired semiconductor substrates with spin casting, Langmuir-Blogdett assembly and transfer, etc. The use of surfactant molecules may deleteriously influence the metal/semiconductor interfaces for applications. As a result, developing simple approaches to efficiently grow metal nanoparticles on semiconductor substrates with clean metal/semiconductor interfaces represents a challenge to synthesize hybrid materials with complex functionalities in nanophotonic applications, such as surface-enhanced Raman scattering (SERS), photoelectrochemical cells for solar energy conversion, and optoelectronics. We have tackled this challenge by combining colloid synthesis, surface chemistry, electrochemistry, and photoelectrochemistry in the last couple of years, leading to a promising progress in controllable growth of anisotropic nanoplates of various metals on semiconductor wafers of both n- and p-types. For example, silver nanoplates with uniform thickness (~25 nm) and different sizes (Figs. 1A and 1B) can be synthesized on highly doped n-type GaAs wafers through simple reactions between an aqueous solution of 1 M $AgNO_3$ and the wafers themselves at room temperature for

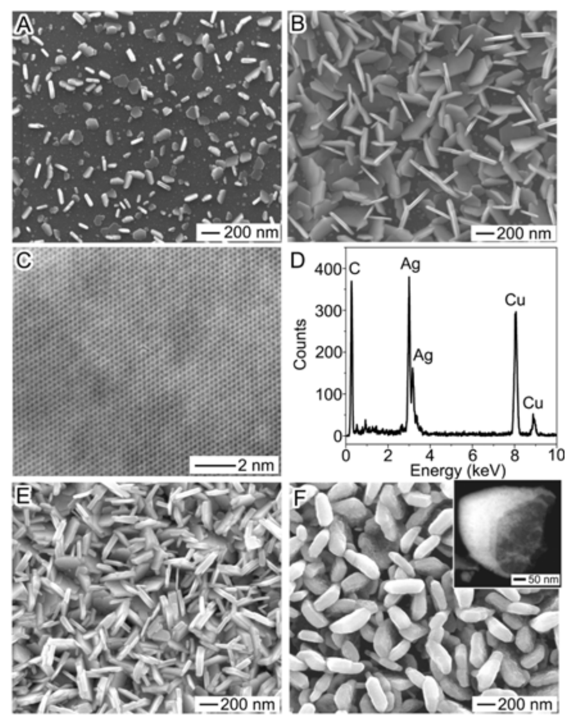

Figure 1. (A, B) SEM images of Ag nanoplates grown on n-GaAs wafers for (A) 0.5 and (B) 2 min. (C) High-resolution TEM image and (D) EDS spectrum of the individual Ag nanoplates shown in (B). (E) SEM image of Ag nanoplates grown on a p-type GaAs wafer. (D) Au/Ag alloy nanoplates converted from the Ag nanoplates shown in (B) through overgrowth.

different growth times. These Ag nanoplates have smooth surfaces and protrude out of the surfaces of the GaAs substrates. Structural (Fig. 1C) and elemental (Fig. 1D) analyses indicate that the as-grown Ag nanoplates are single crystals and are composed of pure silver without any contaminations from the GaAs substrates. With assistance of light illumination, Ag nanoplates can also be grown on p-type GaAs wafers (Fig. 1E). The as-grown Ag nanoplates can be converted to nanoplates made of other components, such as Au/Ag, Pt/Ag, Pd/Ag alloys, through a combination of overgrowth and alloying processes (Fig. 1F).

The Ag nanoplates exhibit interesting optical properties due to their strong surface plasmon resonance (SPR) under photo-illumination. Figure 2A presents extinction spectra of the Ag nanoplates with different sizes in the UV-visible-NIR regions, clearly showing that the major SPR peaks gradually shift to the red with increase of the sizes of the nanoplates. Due to the existence of sharp edges, the Ag nanoplates can serve as a kind of excellent SERS substrates for sensitive detection of molecules close to their surfaces (Fig. 2B).

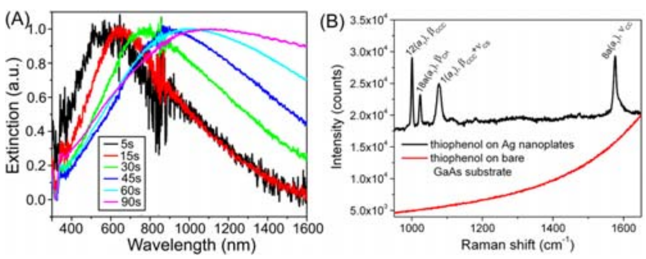

Figure 2. (A) Extinction spectra of the Ag nanoplates grown on n-GaAs wafers through reactions with 2 M $AgNO_3$ solutions for different times. (B) Raman spectra of thiophenol molecules self-assembled on (black) on Ag nanoplates and (red) bare GaAs surface.

Future Work

Future work includes the study of coupling behavior in terms of optical and electrical properties between the metal nanoplates and the semiconductor substrates as well as charge transfer processes at the metal/semiconductor interfaces under photo-excitation. The coupling behavior of these metal nanoplates/semiconductor hybrid materials and interesting dye molecules will also be studied for their photochemical and photoelectrochemical properties.

Publications

"Laser-Driven Growth of Silver Nanoplates on p-Type GaAs Substrates and Their SERS Activity", Sun, Y.; Pelton, M., *J. Phys. Chem. C*, **2009**, *113*, 6061-6067.

"Facile Tuning of Superhydrophobic States with Ag Nanoplates", Sun, Y.; Qiao, R., *Nano Research*, **2008**, *1(4)*, 292-302. (Highlighted as back cover article)

"Formation of Oxides and Their Role in the Growth of Ag Nanoplates on GaAs Substrates", Sun, Y.; Lei, C.; Gosztola, D.; Haasch, R., *Langmuir*, **2008**, *24(20)*, 11928-11934.

"Effects of Visible and Synchrotron X-Ray Radiation on the Growth of Silver Nanoplates on n-GaAs Wafers: A Comparative Study", Sun, Y.; Yan, H.; Wu, X., *Appl. Phys. Lett.* **2008**, *92*, 183109.

"Comparative Study on the Growth of Silver Nanoplates on GaAs Substrates by Electron Microscopy, Synchrotron X-Ray Diffraction, and Optical Spectroscopy", Sun, Y.; Yan, H.; Wiederrecht, G. P., *J. Phys. Chem. C* **2008**, *112*, 8928-8938.

"Direct Growth of Dense, Pristine Metal Nanoplates on Semiconductor Substrates", Sun, Y. *Chem. Mater.*, **2007**, *19*, 5845-5847.

"Surfactantless Synthesis of Silver Nanoplates with Rough Surfaces and Their Application in SERS", Sun, Y., Wiederecht, G. P. *Small*, **2007**, *3*, 1964-1975. (highlighted with cover illustration)