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Synthesis of Novel Plasmonic Materials and Their Optical Properties

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This thesis is dedicated to my beloved family and parents

for always supporting, endless love, and standing by me.

Certificate of Original Authorship

I verify that this submission is my own work and, to the best of my understanding, it does not contain any material previously published by another person, nor material which to a substantial extent has been accepted for the award of any other degree or diploma at any educational institution, except where due acknowledgement is made in the thesis.

Nikta Shahcheraghi

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Abstract

The field of ‘plasmonics’ has gained a lot of attention recently. This is because plasmonic phenomena can be used in a wide variety of modern devices, including biosensors, intracellular probes, spectrally-selective coatings, hyperthermal medical treatments, new kinds of photonic devices, nano-optics, scanning microscopy and optical cloaking. One issue with plasmonics, however, is that the metallic materials currently used cause high losses due to conversion of light to heat. The aim of my project was to discover ways to minimize optical losses in materials and nanostructures used for plasmonics. My search for better materials extended over the pure elements, intermetallic alloys and conventional alloys systems. The most promising example from each of these material types was selected for further examination on the basis of their having a low optical loss over some region of the visible spectrum. The representatives were Ag for the pure elements, $PtAl_2$ for the intermetallic compounds, and α-(Cu,Al) for the metallic alloys.

Silver is considered as one of the most desirable materials for plasmonic devices as it has low loss (low ε_2) across the visible spectrum. Unfortunately, silver nanostructures oxidize or corrode in air. My project started with a study of silver nanotriangles which I synthesized using ‘wet chemical’ techniques. The aim of this part of the project was to discover how fast the silver nanoparticles oxidized and whether some means of preventing the oxidation could be found. I used scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM) and UV-visible spectroscopy to characterize my samples. Unfortunately, while the silver nanotriangles colloids were stable in a sealed bottle for several months, they oxidized within a few days once removed. I did not find a way to prevent this. I did find that silver nanotriangles are able to self-assemble into complex structures that include tip-to-tip or base-to-base, or double- and triple-decker sandwich configurations. The optical properties of these interesting arrangements were explored through computer simulations based on the discrete dipole approximation (DDA). The effect of aspect ratio, gap size and substrate were considered.

It has been predicted in the recent literature that the brassy-yellow $PtAl_2$ intermetallic compound should be capable of exhibiting reasonably strong localized surface plasmon resonances. In this part of my project I investigated ways to fabricate $PtAl_2$ nanoparticles to test this claim. Ordered arrays of $PtAl_2$ semi-shells were created using magnetron sputtering by co-depositing Al and Pt onto a template of

monodisperse spherical polystyrene particles of 300 nm diameter. Deposition was carried out at an acute angle to the substrate so that the resulting semi-shells could be subsequently separated. I examined the resulting material using X-ray diffraction and scanning electron microscope microscopy and the optical properties were probed by measurement of reflection and transmission spectra. I also performed optical simulations based on the DDA. The results showed that the measured properties were consistent with the occurrence of a localized surface plasmon resonance, which proved that $PtAl_2$ could be used in plasmonic applications.

Finally, I considered the example of a metallic alloy, in this case between Cu and Al. The high electron density of Al (three electrons per atom) was expected to be beneficial because addition of Al to Cu would increase the electron-to-atom ratio of the alloy. This would influence the electronic structure and subsequently the dielectric function and Fermi level. Techniques used included ellipsometry, spectrometry, XRD and SEM. Very good results were obtained for an alloy of Cu with 15 at% Al. I also looked at the effect of crystal structure by comparing γ Cu-Al phase in the metastable and stable states. Samples were deposited at room temperature by magnetron sputtering onto a glass substrate (metastable) then annealed at 500°C for 20 minutes (stable). There was a surprisingly big change in optical properties on going from the metastable to stable states, and a region of very low loss was identified in the spectrum.

Overall, the work has proved very successful. While a means to suppress oxidation of Ag was not found, three promising new materials ($PtAl_2$, Cu-15 at.% Al, and Cu-Al γ-phase) were identified for future plasmonic applications.

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