

Switching plasmonic resonances via the hysteretic behavior of SmS piezoresistive thin films

Andreas Sousanis¹, Philippe F. Smet^{1*} and Dirk Poelman¹

¹Lumilab, Department of Solid State Sciences, Ghent University, Krijgslaan 281-S1,
9000 Gent, Belgium

*philippe.smet@ugent.be

SmS is a switchable chalcogenide which shows a pressure-induced semiconductor-metal transition, while the semiconducting state can be restored by annealing. This work reports on the tunable plasmonic resonance in the system SmS-Au, due to the non-spherical shape of gold metallic nanoparticles on top of the semiconducting SmS thin film. Both a constant and a tunable resonance wavelength were obtained. The switching behavior of SmS was accompanied by a reversible switching behavior of the plasmonic resonance modes.

Introduction

The last few years there is a widespread interest in both plasmonic and switchable materials. Plasmonic nanostructures have been proposed for several applications, such as plasmonic-enhanced solar cells, plasmonic LEDs, surface enhanced Raman spectroscopy (SERS) and plasmonic-based photocatalytic structures. [1-4] Localized Surface Plasmon Resonances (LSPRs) result from the resonance between the incident wavelength and the resonant frequency of the free electrons of a metallic nanostructure. This resonance is strongly influenced by both the shape and the size of the nanostructure and the surrounding environment. [4,5] . In this work we report on a system consisting of Au deposited on a switchable SmS film, [6] showing a pressure induced transition from the semiconducting to the metallic state. After annealing SmS-Au, we obtain Au nanostructures with several shapes and sizes, which depend on the annealing time and the Au film thickness. This system can exploit the switching ability of SmS to promote a switching behavior of the plasmonic resonance, as the surrounding environment changes from one state to another.

Experimental details and results

SmS films with thickness 50 nm were grown by reactive e-beam evaporation in an H₂S atmosphere on glass substrates and Si (100) wafers, at a substrate temperature of 230°C and 250°C respectively. The semiconductor to metal transition took place by rubbing the SmS surface with tweezers, without visibly damaging it. In order to switch the films back to the semiconducting state, we used heating under vacuum at 400°C. The Au deposition was carried out using an Emitech coater k550. The ultraviolet-visible spectra were recorded at room temperature in the transmission geometry with a Varian Cary 500 spectrophotometer in the wavelength range 200–1100 nm. Scanning Electron Microscopy (SEM, FEI Quanta FEG 200) was used in order to study the surface morphology of some of the films. Annealing in air was carried out using a muffle furnace Nabertherm LT 9/13/P330.

Fig. 1 shows the optical cross section (Absorption+Reflection) of a SmS-Au bi-layer system on glass. In fig. 1a, the dotted line represents the spectrum of as-deposited SmS in its semiconducting state. [6] By depositing gold via DC sputtering (6 nm of Au) the cross section optical spectrum is seen to increase over the entire wavelength range. By annealing for 15 minutes at 300°C, changes in the optical spectra appear. A similar thin film without the presence of Au shows no change in the spectrum relevant to the appearance of the resonance. Vertical black lines represent the optical transitions of semiconducting SmS. In figure 1b, changes of the SmS-Au spectra are shown for annealing between 15 and 300 minutes. [6] At lower energies, a peak appears, demonstrating the appearance of Au nanoparticles, which support plasmonic resonances. [7] The time in the graphs shows the cumulative time of annealing in ambient air. When the SmS film is annealed at temperatures up to 300°C in ambient air and higher under vacuum, some additional XRD peaks appear, but this does not influence the switching behavior of the material. In order to remove the contribution of SmS from the optical spectra, we divided the transmittance of the SmS-Au film by the transmittance of the as-deposited SmS annealed at the same annealing time (see fig. 3, below), so that the behavior of Au can be monitored separately. [7]

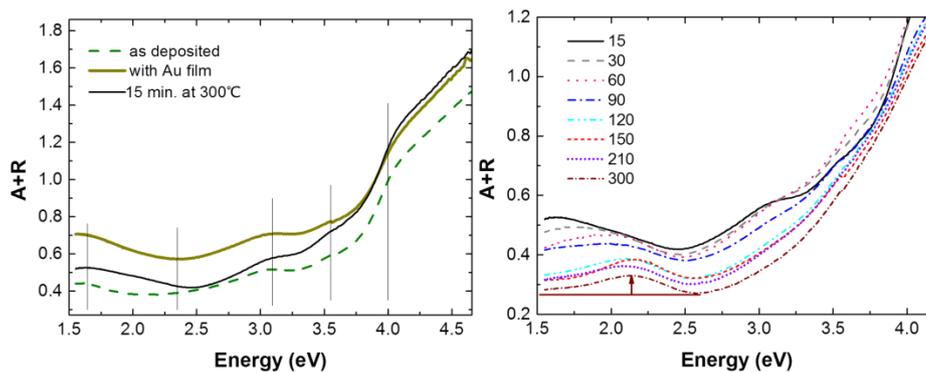


Figure 1. (a) Absorption+reflection spectra of as-deposited SmS, SmS-Au, and SmS-Au after 15 minutes of annealing (thinner line). Vertical lines represent some of the transitions of SmS in the semiconducting state. (b) SmS-Au optical spectrum upon increasing annealing time (times in minutes). Plasmonic resonance is clearly seen.

In fig. 2.a we can see the morphology of an as-deposited SmS (i), the surface of Au deposited on SmS (ii) and the Au nanostructures on SmS after annealing (iii). The first one of the two resonance peaks centered at around 3.75 eV (not shown), remains constant as a function of annealing time, while the second resonance at lower energies is tunable. Additional resonances typically point to nanoparticles, which support more than one degree of freedom, promoting more than one plasmonic resonance mode. [8,9] In our case, this is related to the simultaneous occurrence of particles with several shapes. In case of the tunable resonance we can see a blue shift of the LSPR resonance in fig. 2b. Possible causes of the blue shift are the creation of more spherical nanoparticles upon annealing or a decrease of the number of initially larger Au structures on the surface of SmS. [10,11] In fig. 2c it is seen that the width of the low energy resonance decreases after annealing when the particle size distribution becomes more homogeneous. [12] In addition, the increase of the resonance amplitude and decrease of the width can be interpreted as an increase in the grain size over time

providing a decrease of the grain boundary scattering, which gives rise to plasmon damping. [12]

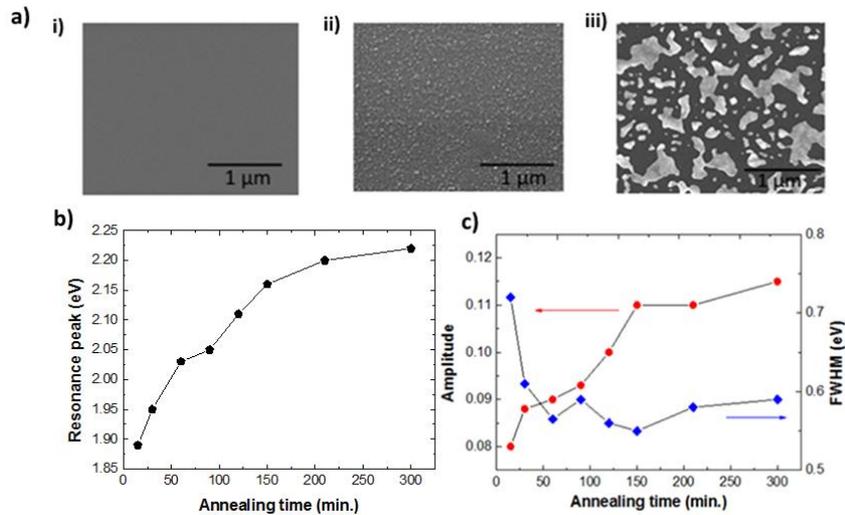


Figure 2. (a) SEM figures of the surface of a SmS thin film (i), the bi-layer of SmS-Au (ii) and the SmS-Au surface after annealing for 120 minutes (iii). (b) Position of the low energy resonance as a function of annealing time. (c) Amplitude (balls) and FWHM (rhombus) of the low energy resonance as a function of annealing time.

Fig. 3 shows how the switching behavior of the SmS leads to switching of the plasmonic resonance. Initially, there is a peak centered at around 2.2 eV, for an annealed thin film at 300°C, for 300 minutes. This peak disappears when the SmS becomes metallic by rubbing its surface with tweezers. By rubbing, SmS switches to the metallic state, and immediately the dielectric function of SmS changes. By annealing the thin film at 400°C under vacuum, SmS switches back to the semiconducting state. Upon the transition of SmS to the metallic state any resonance completely disappears as the changed dielectric function of SmS does not support the plasmonic resonances. The resonance itself is seen to be redshifted after annealing, which could be related to an increase of the size of the Au nanostructures during the redistribution of the Au nanostructures on the SmS film due to rubbing.

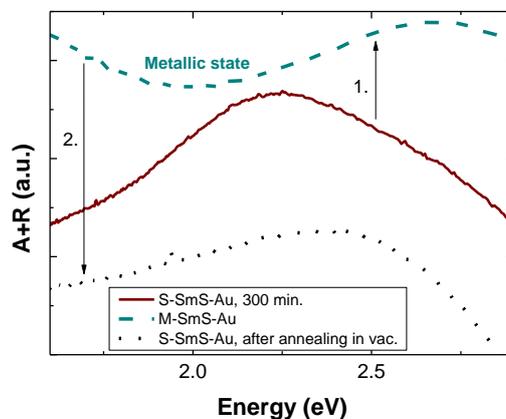


Figure 3. Switching of the plasmonic resonance upon the metal-semiconductor transition (1.: semiconductor - metal transition, 2.: metal - semiconductor transition).

Conclusions

We reported for first time on the behavior of a SmS-Au bi-layer system. The plasmonic resonance, which appeared after annealing the initial SmS-Au bi-layers, can be tuned in the optical spectrum of SmS. An additional resonance appeared related to structures with more than one degree of freedom. Finally, a switching behavior of the plasmonic resonance appeared as a result of the changes of the dielectric function of SmS upon transitions between the semiconducting and metallic states.

Acknowledgments

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