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Characterization and Optical Absorption Properties of Plasmonic Nanostructured Thin Films

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Abstract – Ag (Au)/SiO_2 nanostructured thin films were fabricated on n-type silicon substrates by Radio Frequency (RF) magnetron sputtering technique. Crystalline, surface topography and optical properties of the prepared films were analyzed using X-ray diffractometry (XRD) technique, Atomic Force Microscopy (AFM) and UV–visible spectrophotometry, respectively. Optical absorption spectrum of the Ag/SiO_2 thin films showed one surface plasmon resonance (SPR) absorption peak located at 310 nm relating to silver nanoparticles while the SPR peak in Au/SiO_2 sample experienced a redshift around 450 nm.

Keywords: Ag/SiO_2, Au/SiO_2, thin film, nanostructure, surface Plasmon resonance, sputtering, optical absorption

1. Introduction

Optical absorption by nanoparticles, specifically the noble metals Ag (Au or Cu), is distinctive over the range of visible light [1–5]. Such absorption is due to the resonant oscillation of the conduction band electrons when interacting with an external electromagnetic field [5–7]. This resonance is known as the Surface Plasmon Resonance (SPR). The SPR is a unique physical phenomenon only for nano-size particles, it is absent at scales of atoms or bulk [8, 9].

Nanolayers with metallic clusters or crystals in dielectric matrix have potential applicability for photonics, magnetics and electronics, and single electron devices [10, 11]. In order to fabricate new nano-scale devices with excellent properties, we should choose novel materials and improve the ability to synthesize, deposit, and position nanosized building blocks on suitably designed substrates [12]. So, it plays an important role in the actual application of the nanolayers that we adopt novel materials and advanced techniques in the experiment.

To date there have been many studies on nanolayers which consist of different materials, such as Au/Al_2O_3 [13], Ag/SiO_2 [14, 15], Au/ZnO [16], Au/SiO_2 [17], and ZnO/SiO_2 [18]. Depositing noble metal nanoparticles, such as Au and Ag [19–24], can effectively enhance the absorption capability, given by the surface plasmon resonance (SPR) [25, 26]. In addition, metal nanoparticles can capture the photo-generated electrons, leading to the reduction of the recombination rate [27, 28]. Therefore, the optical absorption capability and photocatalytic activity of metal particles embedded in SiO_2 nanoparticles and SiO_2 nanofibers [29–31] have been investigated widely in the past decades.

Silicon dioxide (SiO_2) thin films are broadly used in various fields such as passivation layers of electronic devices, protection layers of magnetic or optical disks and anti-reflective (AR) coatings of displays, because of their excellent chemical stability and optical transmittance with low refractive index [32–35]. Many methods serve to prepare SiO_2 based coating, such as sol–gel, magnetron sputtering, thermal oxidation, physical vapor deposition, chemical vapor deposition, etc. The physical and optical properties of SiO_2 layer depend on the method of deposition. Among these thin film deposition methods, radio frequency (RF) magnetron sputtering is one of the industrially practiced techniques for preparation of uniform films on large area substrate with required chemical composition.

In this study, we present the preparation and characterization of Ag/SiO_2 and Au/SiO_2 thin films with uniform surface by RF magnetron sputtering method. In our experiment, SiO_2 was first deposited on the n-type Si (silicon) substrate.

Subsequently, Ag (or Au) was deposited on the surface of SiO_2 layer. The Ag/SiO_2 and Au/SiO_2 thin films were characterized by X-ray diffraction (XRD) and Atomic Force Microscopy (AFM) and their optical absorption was measured by UV–VIS spectrophotometer. We observed an enhanced nonlinear optical absorption for each sample due to the surface plasmon resonance of metal nanoparticles.

2. *Experimental*

The Ag/SiO_2 and Au/SiO_2 thin films were deposited on n-type silicon wafer by sputtering technique. In this process the substrates were not heated nor rotated over the target. The main adjustable process parameters are input power, total gas pressure and target-to-substrate distance. For the deposition of SiO_2, the sputtering system was first pumped down to 2×10^{-6} torr then Ar gas (30 sccm) was introduced to fill the chamber up to 3×10^{-3} torr. A 40 V bias voltage was applied to the substrate for 10 min in order to clean the substrate surface. After 10 min, the bias was switched off and the deposition started with a supply of oxygen gas at 1.5 sccm. During deposition, the power of Si (99.995% purity) target was kept at 500 W (RF) and the sputtering rate about 1.1 Å/s. When the deposition of SiO_2 film finished, the deposition of Ag (Au) film started. Throughout the process, a 100 W (DC) sputtering power was kept at Ag (or Au with 99.999% purity) target with sputtering rate around 9.5 Å/s. A target-to-substrate distance of 120 mm remained unchanged during the whole process. The thickness is confirmed by surface profiler after the sputtering. Parameters for the control of deposition of SiO_2 and Ag (Au) films are listed in Table 1 for readers' reference.

Table 1

Parameters for deposition of SiO_2 and Ag (Au) films on Si substrate by sputtering.

Parameters for Sputtering	SiO_2 on Si substrate	Ag (Au) on SiO_2 and Si substrate
Background pressure	$2\times10^{-6}\,Torr$	$2\times10^{-6}\,Torr$
Working pressure	$3\times10^{-3}\,Torr$	$3\times10^{-3}\,Torr$
Working gas flow	Ar : 30 sccm O_2 : 1.5 sccm	Ar : 30 sccm O_2 : 1.5 sccm
Sputtering power	(RF): 500 W	(DC): 100 W
Sputtering rate	1.1 Å/s	9.5 Å/s
Substrate temperature	25 C°	50 C°
Average thickness	10 nm	40 nm

The fabrication steps of Ag (Au)/SiO_2 thin films could be seen in Fig. 1.

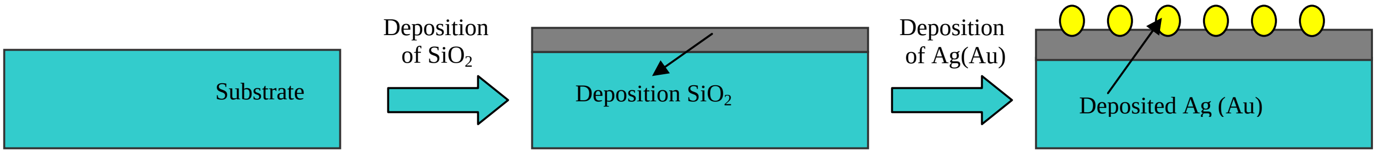


Fig.1. Schematic drawing for fabrication process.

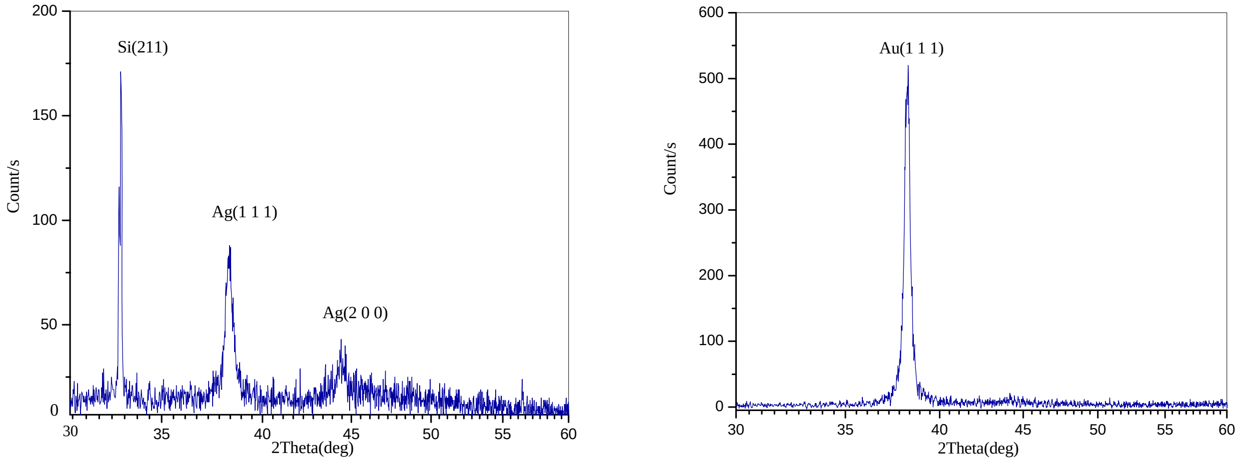
As shown in Fig. 1, SiO_2 was first deposited on the substrate. Subsequently, Ag (or Au) was deposited on the surface of the SiO_2 layer. The Ag (or Au) particles were entirely exposed with uniform distribution on SiO_2.

The crystallographic structure of the films was determined with X-ray diffraction taken on an X' Pert Philips using monochromatic Cu-Kα radiation. The surface morphology and roughness of the films were analyzed with the atomic force microscope (Dynamic-AFM, Dualscope/rasterscope C26, DME, Denmark). The optical absorption of the films was recorded using UV-visible spectrophotometer (Cary 6000i) in the 200-1200 nm wavelength range.

3. Results and discussion

a) Structural properties

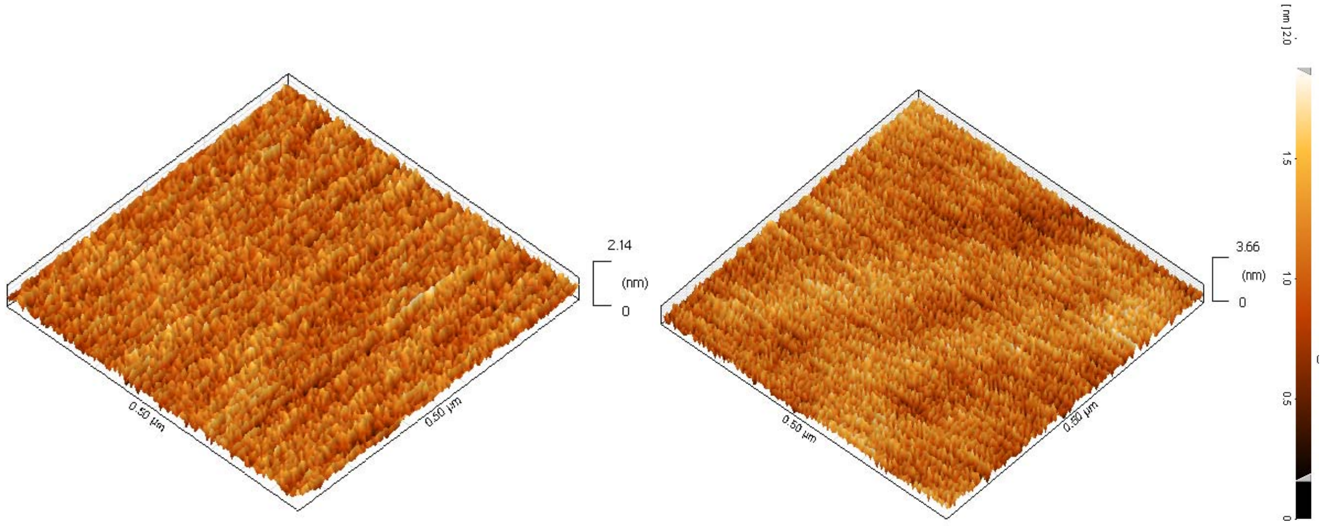
The crystalline structure of the Ag/SiO_2 and Au/SiO_2 thin films were investigated by X-ray diffractometry. The X-ray diffraction spectra for both nanostructured samples are presented in Fig.2. For Ag/SiO_2 thin film three peaks were observed at 33.2, 38.3 and 44.4 which correspond to Si (2 1 1), Ag (1 1 1) and Ag (2 0 0). The peak of Si (1 1 1) can be attributed to the Si substrate. However, for Au/SiO_2 only one strong diffraction peak Au (111) was observed. No peaks belong to as deposited SiO_2 are found in both samples, because SiO_2 is amorphous during the preparation. The mean diameters (D) of particles were estimated using a well-known Scherrer's formula [36]. The calculated Ag and Au particle mean size was found 30 nm and 61nm, respectively.



(a) (b)

Fig.2. XRD patterns of (a) Ag/SiO_2 and (b) Au/SiO_2 thin films

Fig.3 shows the AFM images of the thin films. As shown in these figures, continuous and regular films were formed, without significant changes in morphology. AFM images illustrate that the particles growth on substrate was quite regular, and the size of particles was fairly uniform. The root-mean-square (RMS) of the films was measured by AFM over the area of 0.5×0.5 μm which are 0.27 nm and 0.54 nm for Ag/SiO_2 and Au/SiO_2 on n-type Si wafer, respectively.



(a) (b)

Fig.3. AFM topography images of: (a) Ag/SiO_2 and (b) Au/SiO_2 nanostructured thin films

b) Optical properties

Below of the Si substrates are tarnished, so there are not any transitions. The reflection spectrum of the films has been recorded at room temperature by spectrophotometry. Fig.4 shows reflection curves against wavelength for Ag/SiO_2 and Au/SiO_2 thin films.

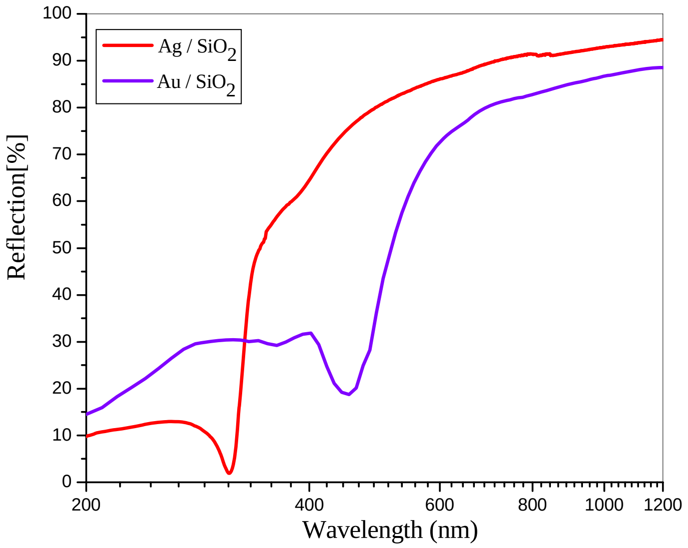


Fig. 4. Reflection versus wavelength for Ag/SiO_2 and Au/SiO_2 thin films

The optical absorption is calculated afterwards by subtracting reflectance of Ag (Au) film from 100%. Fig. 5 shows absorption curve against wavelength for Ag/SiO_2 and Au/SiO_2 thin films.

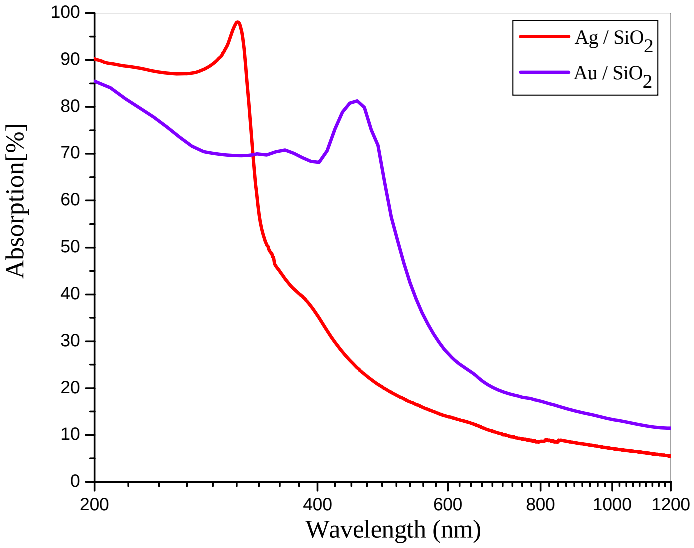


Fig. 5. Absorption versus wavelength for Ag/SiO$_2$ and Au/SiO$_2$ thin films

The absorption spectrum reveals low absorbance in the visible and near infrared regions for Ag/SiO$_2$ sample. However, absorbance in the ultraviolet region is significantly high and the sample exhibits an obviously enhanced optical absorption property at 310 nm. This significant increase could be attributed to the plasmon resonance absorbance of the Ag nanoparticles, since the noble metal nanoparticles can be photoexcited due to their plasmon resonance. This high absorbance in the UV region makes this material important in photovoltaic technology. On the other hand, the absorption spectrum demonstrates a broad and red-shifted absorption peak for Au/SiO$_2$ sample. For this sample, a broad surface plasmon resonance (SPR) absorption peak is observed at 450 nm with a shoulder at 360 nm. The appearance of this shoulder is generally associated with the presence of either oblate spheroid particles or closely aggregated spherical particles that optically behave as oblate spheroids [36-38]. This latter possibility is however thought to be the most plausible situation in our films because there is no evident reason to form specifically oblate particles. Moreover, one cannot exclude that the broadness of the SPR peak might be also due to some size distribution of metal nanoparticles.

4. Conclusions

Ag/SiO$_2$ and Au/SiO$_2$ nanostructured thin films with uniform surface were prepared by radio frequency magnetron sputtering technique. The characterization of thin films was carried out by XRD, AFM and UV-VIS. From the XRD results, Si (2 1 1), Ag (1 1 1) and Ag (2 0 0) planes were observed and also the strong diffraction intensity of Au peak occurred. The AFM indicate that the surfaces of films are uniform and well-distributed Ag (or Au) particles were formed in nanostructured film. Nonlinear optical absorption peaks due to the surface plasmon resonance are observed for all films. For Ag/SiO$_2$, the enhanced optical property is located in the ultraviolet region (310 nm) while Au/SiO$_2$ experienced broaden and red-shifted absorption peak in the visible region (450 nm). The present results open a possible way to design and fabricate photocatalysts and solar energy devices.

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