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SURFACE ENHANCED INFRARED ABSORPTION FROM $Ge_{20}Se_{70}Te_{10}$ FILM WITH SILVER ISLAND OVER LAYER

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ABSTRACT

Infrared absorption is a highly selective technique for the identification of specific chemical compounds. Thin metallic layers or nanostructures on the IR transparent substrate or host is found to increase the IR absorption capability of the attached molecules due to the surface plasmon resonance from these metal surfaces. This phenomenon is known as surface enhanced infrared absorption (SEIRA). For developing superiorinfrared sensing platforms, betterhost materials are required. In this work we report on the development of a SEIRA platform from a chalcogenide glass- silver combination to show that this infrared material can be used for SEIRA spectroscopy. Here silver island structures were developed on both plane silica substrate and $Ge_{20}Se_{70}Te_{10}$ glass coated silica substrates via oblique angle deposition technique. The presence of island structures is confirmed with the help of SEM and UV/Vis/NIR absorption spectra. To assess the performance of the substrate, a self-assembled monolayer of Hexadecanethiol (HDT) is used and its response is analysed with FTIR spectroscopy. These preliminary results are promising and will pave way for developing various advanced sensor configurations.

KEYWORDS: SEIRA, Chalcogenide Glass, IR Spectroscopy, GeSeTe Glass.

IR spectroscopy isa very powerful technique for characterizing molecules and chemical reactions. The great molecular selectivity and identification of specific chemical compound allow them for detection of chemical and biological species both qualitatively and quantitatively.Even though this non-destructive non-invasive technique has the potential to compete with other composition analysis methods like XPS, EDS etc.,it is suffering from its low detection limit. A promising solution to enhance the sensitivity of IR spectroscopy is reported by Hartstein and co workers for the first time in their 1980 paper (Hartstein et al; 1980), according to which molecules attached to or placed veryclose to metal island structures are expected to give an enhanced infrared absorption. This is termed as surface enhanced infrared absorption (SEIRA)(Osawa; 2002). Surface Plasmon Resonance (SPR) from metal surfacesare the key mechanism responsible for this enhanced IR absorption. As the SPR frequency can be tuned with metal type, size, shape etc.several studies have conducted since its first discovery withdifferent metals (Au, Cu, Ag, Pt), of various morphologies (films, nanorods, nanoshells).In order to access the vibrational fingerprint absorption of the organic molecules via SEIRA, optical waveguides or substrates on which these metal nanostructures are fabricated must be having high transparency in the IR region.Even though there are reports inferring the significance of substrate properties on SEIRA response (Nishikawa et al; 1993) very less attention is drawn into developing better substrate for IR spectroscopy. Most commonly used substrates are crystals of CaF_2,Ge or Si which cannot be easily shaped into integrated optical devices devoted to mid infrared (Verger; 2012). Chalcogenide glasses are promising host for the same as they are highly transparent in this region.Chalcogenide glasses can be transparent up to 20µm depending upon the composition (A.B. Seddon; 1995). In addition to this, they have flexibility in fabricating waveguide structures like optical fibers, planar wave guides, photonic band gap structures etc for developing advanced sensor platforms.

In this paper, we report on the development of SEIRA substrate from a chalcogenide glass thin film of composition $Ge_{20}Se_{70}Te_{10}$. Silver island structure was fabricated on the surface of the chalcogenide film via oblique angle deposition. The SEIRA enhancement from the substrate is analyzed by recording the spectral features of HDT molecule attached to themetal surface using FTIR spectrometer.

MATERIALS AND METHODS

Chalcogenide glass of composition $Ge_{20}Se_{70}Te_{10}$ is prepared by conventional melt quench method. Thin films of $Ge_{20}Se_{70}Te_{10}$is fabricated by thermal evaporation on silica glass substrate at a pressure of 3.7×10^{-5} mbar. The thickness of the film was calculated to be 1.26µm. For enhanced infrared absorption thin silver nano films are fabricated on both plane and chalcogenide glass surfaces by oblique angle deposition using thermal evaporation technique (Sobahan; 2010). The coating is carried out in a vacuum chamber at 2.9×10^{-5} mbar pressure. 99% pure silver piece is loaded in a Tungsten(M.P. 3422^0C) boat and evaporated via resistive heating by applying 10A current. The Substrate was tilted at 55^0 and the source to coating surface center distance was kept to be 16cm. The rate and

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thickness of the deposition are recorded with the help of thickness monitor associated with the vacuum coating system. The deposition rate was fixed at 0.2 A°/sand coating thickness obtained was 5.4nm.

HDT (mol weight: 258.51 g/mol and density 0.84g/ml) was purchased from Sigma Aldrich and kept in therefrigerator to reduce its degradation. For self-assembled mono layer fabrication, 0.03 ml of HDT is dissolved in 15 ml ethanol by sonicating the sample for 5 minutes. 8μl of this solution is drop casted on the OAD silver island films using a micropipette and allowed to dry at room temperature. The IR spectra of the HDT coated $Ge_{20}Se_{70}Te_{10}$ films with and without silver nanostructure is recorded using Thermo Nicolet, Avatar 370 FTIR spectrometer with DTGS detector in transmission mode.

RESULT AND DISCUSSIONS

Silver nanostructures were deposited both on aplane and $Ge_{20}Se_{70}Te_{10}$glass coated silica substrates. Silver shows poor adhesion tosilica substrate such that the film damaged even with a very slight mechanical contact. Whereas $Ge_{20}Se_{70}Te_{10}$ film shows good adhesion to silver. This increased adhesion capability of silver on Chalcogenide glass provide anadvantage in fabricating devices devoid of adhesion layers (such as Ti) used with acommon substrate like silicon (Dong et al; 2017).

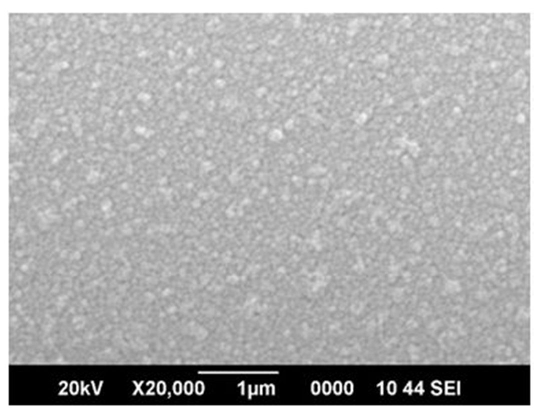
The surface morphology of the deposited silver nanostructure is analyzed with the help of SEM (JEOL Model JSM - 6390LV) analysis. The image of silver nanostructures on theplane glass and GeSeTe film are provided in Figure 1. From the figure, it is visible that the silver evaporated on the surface is not continuous but is composed of nanostructured islands.

Figure 2 a shows the UV/Vis/NIR absorption spectra of silica glass plate coated with silver. The absorption peak of the same is located at 590nm and its tail is extending upto NIR.In the visible spectral region, there is a broad and intense peak corresponding to the localised surface plasmon resonance of silver islands formed.The broadening and IR tailing is atributed to the dipole interaction occuring between islands (Masatoshi; 1997).

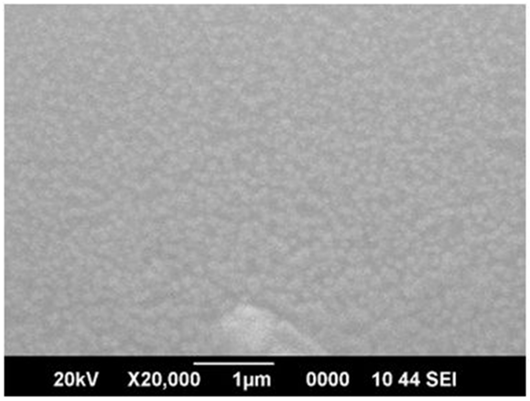
Figure 2b is the UV/Vis/NIR absorption spectra of chalcogenide glass film with and without silver islands with plane glass slide as areference. Both these film shows well resolved Fabry- Perot fringes.In bare ChG film, the fringe pattern is attributed to the interference of two light waves reflected by substrate surface and the ChG/air interface.On the other hand, phase matching condition between two light waves reflected by the substrate surface and ChG/air interfacewas strongly modulated by silver layer, as the refractive index of this layer changes drastically around 500 to 1500 nm due to SPR (Hiep; 2009).

Molecules both chemisorbed or physisorbed shows SEIRA, but due to the strong bonding between adsorbent and adsorbate, chemisorption will provide a larger response. Biological molecules with apolar group can be directly chemisorbed on metal surfaces but molecules without polar group require anchor molecules to do the same. These anchor molecules will attach to the metal surface and form aself-assembled monolayer and will act as aholder for the biological molecules (Michelle; 2001). To assess the performance of the substrate, a self-assembled monolayer of Hexadecanethiol (HDT) is used and its response is recorded with FTIR spectroscopy.For comparison at first, a reference spectrum was aquired from the condensed slurry of HDT dispersed in KBr pellet (Figure 3).There are two dominant /strong absorpion peak around 2924 (CH_2 antisymmetric stretch) and 2855 (CH_2 symmetric stretch). So thesetwo strong peak region is focused on further analysis.

The infra-red transmission spectrum ofHDT molecule (~ 6 mM) adsorbed on OAD silver on $Ge_{20}Se_{70}Te_{10}$ film substrate is given in figure 4. The spectrum is magnified to see the changes in the strong absorption region. The IR spectrum of HDT molecule coated on $Ge_{20}Se_{70}Te_{10}$ film in the presence of silver island structure shows an enhanced IR absorption compared to that of uncoated one. Since the size of HDT molecules is very small (~2.4nm) imaging of SAM layer is very difficult.

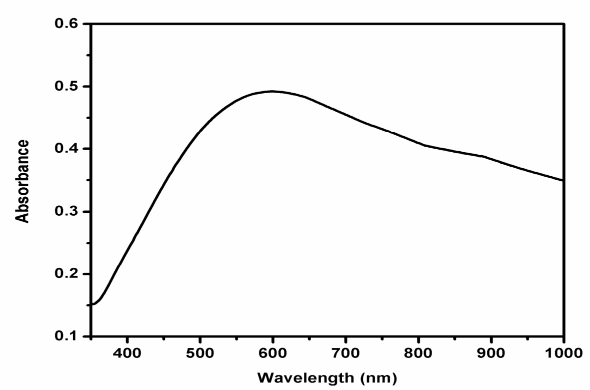


(a)



(b)

Figure 1: SEM image of a) Silver islands on plane glass slide and b) silver islands over $Ge_{20}Se_{70}Te_{10}$ film



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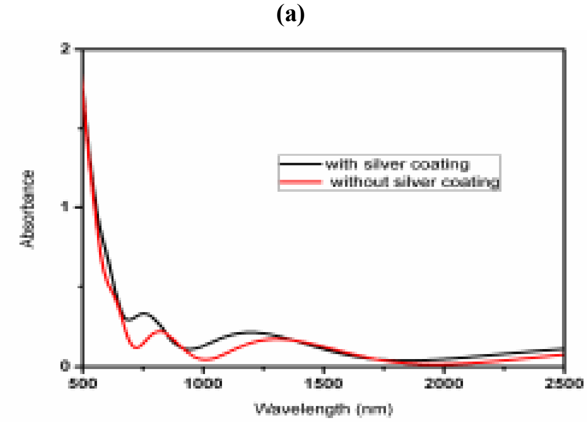

(b)

Figure 2: UV/Vis/NIR spectra of a) silver island coated on aplane glass slide and b) GeSeTe films with and without silver islands

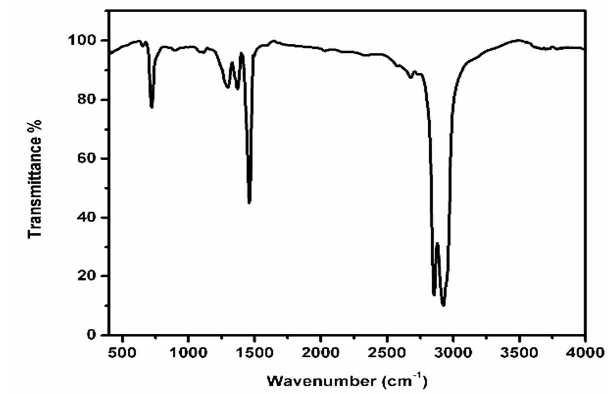

Figure 3: FTIR transmittance spectrum of HDT dispersed in KBr pellette

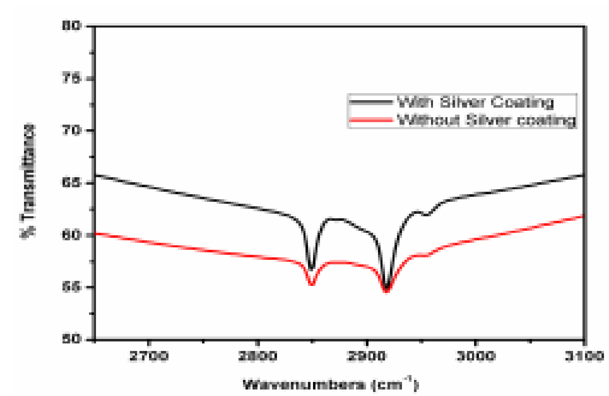

Figure 4: The magnified view of the sensitive region in infrared transmission spectrum of HDT molecules, adsorbed on $Ge_{20}Se_{70}Te_{10}$ glass film substrate with (black) and without (red) silver over layer

CONCLUSION

In this study, we have investigated the usefulness of GeSeTe chalcogenide glass as asubstrate for SEIRA spectroscopy by fabricatingsilver island structures on $Ge_{20}Se_{70}Te_{10}$ film coated silica substrate. For comparison, silver islands are made on both bare and ChG coated silicavia oblique angle deposition method. The formation of island structures is confirmed from SEM and UV/Vis/NIR absorption spectra. Self assembled monolayer of HDT is fabricated on $Ge_{20}Se_{70}Te_{10}$ films with and without silver overlayer and IR spectra are recorded. The enhanced IR absorption from silver coated GeSeTe filmalong with its better adhesion to silver proves it to be a promising candidate as asubstrate for SEIRA. Though the enhancement factor achieved by this islands are very low, by incorporating thismaterial with higher enhancement factor providing structures like IR antennas (electric filed enhancement upto 10^6reported (Liang D; 2017)) it would then be possible to develop integrated optical waveguides for very sensitive SEIRA spectroscopy.

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