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Planar chalcogenide glass waveguides for IR evanescent wave sensors

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Abstract

Multi-layered chalcogenide glass waveguide structures have been fabricated for evanescent wave sensing of bio-toxins and other sensor applications. Thin films of Ge containing chalcogenides have been deposited onto Si substrates, with a-$GeSe_2$ as the lower cladding layer and a-GeSbSe as the core layer, to form the slab waveguide. The absence of a defined upper cladding layer enhances the leakage necessary to sense the target molecules. Modal refractive index is estimated from the m-lines. It is shown that photo-induced structural changes by 808 nm laser light in the core layer selectively enhance refractive index in the exposed regions, and thus provide a convenient method to form channel waveguides. A thin layer of Au has been deposited on top of the core layer for the attachment of linker molecules for biosensor application; ATR confirms this.

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Keywords: Sensors; Planar waveguides; Vapor phase deposition; Chalcogenides

1. Introduction

Among optical sensing schemes, mid-IR fiber-optic sensors are gaining attention because their inherent molecular selectivity allows both qualitative and quantitative analysis of various chemical and biological samples [1]. Waveguides and fiber-optic materials, transparent in the mid-IR spectral region, offer access to fundamental vibrational fingerprint absorptions of organic molecules. The availability of mid-IR waveguides has helped to convert benchtop-style optical instruments such as the FTIR spectrometer into portable compact biological and biomedical optical sensors with higher sensitivity. For example, Afanasyeva et al. [2,3] have used a fiber optic evanescent-wave sensor to help diagnose breast cancer. Bruch et al. [4] have investigated various ways of utilizing mid-IR fiber optic sensosr in dermatology.

One of the important properties of chalcogenide glasses is their high transmission in the infrared region of the spectrum, which makes them particularly suitable for active and passive IR devices. Although various III–V semi-conducting materials are being used in infrared devices, there are various drawbacks of those materials, especially the complex etching process required for the fabrication of channels and cost. Amorphous chalcogenides, especially Ge containing chalcogenides, are less toxic, can be fabricated over large areas by inexpensive evaporation techniques and are easy to handle. Also, the unique set of photoinduced effects in amorphous chalcogenides provide additional functionality for optical fabrication and performance; e.g., the optical band gap and the refractive index can be modified by illumination [5]. Using photo-induced effects, optical elements for applications in

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communications, interconnections, and data storage have been patterned in chalcogenides glasses simply by illumination [6]. Here, we show that the photo-induced changes in refractive index in the illuminated region of a film can be useful for selective writing of channels to create a planar waveguide sensor platform. This process is much simpler and cost effective than the chemical etching process employed with III–V semiconductors.

A hindrance to the use of chalcogenide glasses is their fragility; chalcogenide glasses are easily damaged mechanically and chemically compared to oxide glasses and III–V semiconductors. Also, the coefficient of thermal expansion of chalcogenide glasses is typically an order of magnitude higher than many technologically important semi-conducting substrates used in active devices, which can introduce thermal stresses and adversely affect device performance [7]; some remedies, e.g., rapid thermal annealing, have been proposed to reduce the thermal stress and fabricate high quality films. Despite these drawbacks, the advantages of chalcogenide glasses have led to their commercial use in optical fibers [8] and intense research activity in both fiber and thin films structures for applications in the infrared region [9,10].

In this paper, we report the fabrication of low loss multilayer Ge-based chalcogenide waveguides for evanescent wave sensing. Channels were written on the planar waveguides by illumination and the waveguides were tested for their wave-guiding properties. To utilize the chalcogenide glass for biological target detection, functionalization protocols were developed to attach linker molecules to the waveguide surface for subsequent attachment of anti-body capturing agents. Although various functionalization/activation methods have been developed for silica-based glasses [11], the non-oxide nature of chalcogenide glasses requires different linker molecules. In this work, we have developed a functionalization procedure utilizing gold-thiol chemistry [12].

2. Experimental

Commercially available bulk chalcogenide glasses were used as source materials to deposit thin films of a-$GeSe_2$ (thickness $\sim$2 μm) on clean Si substrates to form the lower index 'bottom' cladding layer, and a-GeSbSe layer (thickness $\sim$5 μm) to serve as the higher index core layer of a slab waveguide. The films were deposited by thermal evaporation, consecutively at $\sim 10^{-6}$ Torr without breaking the vacuum to give a contamination free interface between the two layers. Thin films of the core and cladding compositions were also deposited on microscopic glass slides and silica glass substrates for optical characterization. The deposited films were not annealed.

For writing channels of various dimensions, the slab waveguides were illuminated with a 808 nm semiconductor diode laser through a specially designed chromium mask for 2–3 h in air. The written channels were visually confirmed by optical microscopy.

The optical properties, viz. optical band gap, optical thickness, absorption coefficient and the refractive index, of the films were estimated from the transmission spectra of the films deposited on silica substrates. The changes in the refractive index, induced by laser illumination, in the written parts of the slab waveguide (core layer) were determined from the transmission spectra obtained at the illuminated and the un-illuminated parts of the sample.

The guiding of light through the waveguide was verified by fire end coupling of 1560 nm light through a single mode fiber. In and out coupling of the light at the waveguide was performed by a 20× microscope objective. The light from the fiber was focused and coupled at the edge of the waveguide and the output was imaged by an infrared camera. The incoming light, the waveguide and the outgoing light were aligned with the help of XYZ translational stages.

The ultimate objective of this work is to develop biosensor with high selectivity. To fulfill this goal, we need to functionalize the film with biological molecules that serve primarily as capturing agents for the target molecules to be detected. Eventually, the capturing event can be detected by monitoring the changes in IR spectra before and after binding. Due to the difficulty posed by the GeSbSe chemistry, functionalization strategy through gold films was conceptualized. Accordingly, very thin gold layer ($\sim$20 nm) was deposited on top of the GeSbSe core layer. Anchor molecules (3-mercaptopropronic acid, MPA; and 16-mercaptohexadecanoic acid, MHA) were then attached to the gold to form self assembled monolayers (SAM) to which antibodies are to be attached. The anchor molecules have a –SH tail that bonds to the gold islands and a –COOH head pointing upwards from the surface, to which capturing agents (e.g., human IgG) can be attached.

Generally, capturing agent molecules are large compared to the thiol-compounds (MPA or MHA) used for SAM, hence spatial blocking effect between capturing molecules might cause problems. To minimize this possibility, SAM was built via two types of thiol-compounds: MPA that has a 3-carbon chain and MHA that has a 16-carbon chain, with a ratio of MPA:MHA = 4:1. The SMA so formed should have one MHA for every 4 MPA molecules on average. The longer MHA is expected to serve as anchor for the capturing molecules, since they are sparsely distributed, and spatial blocking would be minimized. A mixture of ethanol solution of 4:1 MPA:MHA was made and the films with gold islands were immersed into this solution for 24 h to allow the SAM to form. Subsequently, the non attached solution was washed away. The attachment of the SAM was confirmed by FT-IR microspectroscopy.

3. Results and discussion

For low loss waveguides to be used for sensing in the infrared region, one of the main criteria is the low absorption coefficient in the targeted range of the spectrum. Chalcogenide glasses transmit well in the mid to far infrared region of the spectrum with a low absorption coefficient.