Integrated photonics for infrared spectroscopic sensing

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Integrated photonics for infrared spectroscopic sensing

Hongtao Lin, Derek Kita, Zhaohong Han, Peter Su, Anu Agarwal, et al.
Integrated photonics for infrared spectroscopic sensing

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ABSTRACT

Infrared (IR) spectroscopy is widely recognized as a gold standard technique for chemical analysis. Traditional IR spectroscopy relies on fragile bench-top instruments located in dedicated laboratory settings, and is thus not suitable for emerging field-deployed applications such as in-line industrial process control, environmental monitoring, and point-of-care diagnosis. Recent strides in photonic integration technologies provide a promising route towards enabling miniaturized, rugged platforms for IR spectroscopic analysis. Chalcogenide glasses, the amorphous compounds containing S, Se or Te, have stood out as a promising material for infrared photonic integration given their broadband infrared transparency and compatibility with silicon photonic integration. In this paper, we discuss our recent work exploring integrated chalcogenide glass based photonic devices for IR spectroscopic chemical analysis, including on-chip cavity-enhanced chemical sensing and monolithic integration of mid-IR waveguides with photodetectors.

KEY WORDS: spectroscopy, optical sensors, optical resonators, infrared sensors, chemical sensors

1. INTRODUCTION

Infrared spectroscopy probes the phonon vibrational states of molecules by measuring wavelength-dependent optical absorption in the mid-infrared regime (2-25 \( \mu \text{m} \) wavelength or 400-5,000 cm\(^{-1} \) in wave number). IR spectroscopy is widely recognized as the gold standard for chemical analysis given its superior specificity: molecular species can be uniquely identified with their characteristic optical absorption bands. Such a “fingerprinting” capability makes IR spectroscopy an ideal technology for applications involving chemical analysis in complex environments, such as industrial process control, environmental monitoring, food quality assessment, forensics, and remote sensing.

Traditional IR spectroscopy relies on bench-top instruments such as Fourier Transform Infrared (FTIR) spectrometers located in dedicated laboratories. These instruments are of the size of large desktop computers and easily cost over $100K. Further, robustness of these systems is often compromised by fragile mechanical moving parts or stringent optical alignment requirements. Recent strides in photonic integration have envisioned standalone "sensor-on-a-chip" platforms capable of performing chemical analysis with minimal power consumption and improved throughput compared to their conventional benchtop counterparts. In addition to the apparent advantages in size, weight, and power (SWaP), no optical alignment is necessary between lithographically defined components in integrated photonic modules, thereby improving

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both manufacturing throughput and system ruggedness. Planar photonic integration further opens up the possibility of cost reduction leveraging standard high-volume semiconductor manufacturing processes for applications such as integration with consumer electronics.

One standing challenge in realizing such integrated photonic "sensor-on-a-chip" platform is the lack of suitable material and component technologies for operation in the mid-IR spectral range. Passive photonic components need to be made from optically transparent materials in the mid-IR. Since silica becomes opaque at wavelengths longer than 4 μm, mid-IR integrated resonators demonstrated to date either involve special suspended designs[1-9] or new material platforms, such as silicon-on-sapphire[10-16], silicon-on-nitride[17-20], or germanium-on-silicon[21-26]. Active optoelectronic devices rely on narrow-bandgap semiconductors to enable operation at mid-IR wavelength, although lattice mismatch of these semiconductors generally prohibit their epitaxial growth and integration on silicon, and therefore heterogeneous integration of III-V semiconductors or graphene have been demonstrated as an alternative route to resolve the challenge[27-30].

Here we propose and demonstrate a mid-IR integrated photonic platform based on chalcogenide alloys, namely the amorphous or polycrystalline compounds containing S, Se and/or Te. The amorphous chalcogenide compounds, i.e. chalcogenide glasses (ChGs) are known for their broadband transparency covering the entire mid-IR band, high and continuously tunable refractive indices (n ~ 2 to 3.5), and large Kerr nonlinearity[31-40]. In addition to their exceptional optical properties, ChG’s are also uniquely poised for mid-IR multimaterial photonic integration. These glasses can be deposited at high rates exceeding 100 nm/min via simple single-source thermal evaporation with the substrate held near room temperature[41] or via simple solution processing[42-45]. Combined with their amorphous nature, good van der Waals adhesion to different substrates without surface modification[46], and ease of processing[47], the extremely low thermal budget allows epitaxy-free ChG coating to form optically thick films on different substrates including silicon and III-V semiconductors, the dominant substrate platform for most mid-IR photonic devices. On the other hand, lead and tin chalcogenides are semiconductors suitable for mid-IR detection. Unlike other narrow-bandgap semiconductors which mandate epitaxially grown single crystals for device fabrication, the polycrystalline form of these chalcogenide semiconductors offer performance comparable or even superior compared to their single-crystalline counterparts due to a unique charge-separating mechanism at grain boundaries[48-51]. These polycrystalline chalcogenides can be readily deposited via chemical bath deposition[52, 53] or thermal evaporation, facilitating monolithic integration of active mid-IR photonic devices on common semiconductor or dielectric substrates[54-56]. Our previous work has developed deposition and processing of these chalcogenide materials and fabrication protocols of photonic devices operating at near-IR telecommunication wavebands on silicon as well as unconventional substrates such as polymers[57-68]. In this paper, we present mid-IR photonic integration based on chalcogenide materials as well as sensing applications of the chip-scale mid-IR photonic platform.

2. CHALCOGENIDE GLASS-ON-SILICON PHOTONICS

In recent years, a series of chalcogenide glass-based mid-IR on-chip photonic devices have been demonstrated leveraging the broadband infrared transparency of the material, signifying the significant growth potential of this research field[69-
Here we chose to fabricate the ChG mid-IR photonic devices combining optical lithography and lift-off, a simple and versatile technique applicable to a wide variety of ChG compositions. Below we illustrate the process when applied to ChG mid-IR waveguide-coupled resonator fabrication[77], although the process is generic and can be equally implemented to other ChG on-chip device processing. The devices were fabricated on (100) silicon wafers topped with 300 nm thermal oxide as the starting substrate. To prevent absorption of silica and optical leakage into the silicon substrate, a 3 μm thick mid-IR transparent (up to 12 μm wavelength) and relatively low refractive index (∼2.1) Ge23Sb7S70 glass film was first deposited as the bottom cladding. Reversed patterns in a negative tone photoresist (NR9- 1500PY, Futurrex Inc.) were defined using contact lithography on an ABM Mask Aligner, and a 1.1 μm thick As2Se3 film was subsequently deposited as the waveguide core layer. The entire structure was then sonicated in acetone to dissolve the resist layer beneath the undesired parts of the As2Se3 film, leaving an As2Se3 pattern reverse to that of the photoresist. As a final step, a 2 μm thick Ge23Sb7S70 overcoating layer was deposited on top of the As2Se3 core to prevent surface oxidation and formation of large AsOx crystallites[58]. To facilitate optical coupling into and out of the bus waveguides, the processed wafers were subsequently cleaved to form end facets.

Fig. 1. Schematic fabrication process flow for the As2Se3 mid-IR waveguides (not drawn to scale).

Mid-IR transmission characteristics of the resonators were measured using a fiber end fire coupling method. Figure 2 illustrates a schematic diagram of the mid-IR measurement setup. In our measurements, a CaF2 lens (NA ~ 0.25) was used to couple TE polarized mid-IR light from a 5.2 μm external cavity tunable quantum cascade laser (Daylight Solution, Inc.) into a customized InF3 fiber (IRPhotonics Inc.). Since the optical fiber is multi-mode at the 5.2 μm wavelength (core/cladding diameters 40/150 μm), careful optimization of the laser-fiber alignment was performed to minimize excitation of high order fiber modes. The mid-IR light was butt coupled to the planar As2Se3 bus waveguides through the optical fiber (Fig. 3a), and optical output at the waveguide end facet was collected by another CaF2 lens and imaged in the far field using a liquid nitrogen cooled InSb Focal Plane Array (FPA). To minimize thermal radiation noise from the ambient background, a liquid nitrogen cooled band pass filter centered at 5.2 μm wavelength was inserted in the optical path.
Fig. 2. Mid-IR fiber end fire waveguide measurement setup schematic.

Fig. 3. (a) Top-view microscope image of a mid-IR InF₃ fiber end-coupled to an As₅Se₃ waveguide with a lateral taper to reduce the mode mismatch; (b) far-field image of the TE guided mode from a single-mode As₅Se₃ bus waveguide; (c) optical microscope top-view image of a 200 μm radius mid-IR resonator; (d) microscope image showing the 2.75 μm wide coupling gap between the bus waveguide and the micro-disk resonator; (e) simulated field intensity profile of the fundamental whispering gallery mode of the ChG micro-disk resonator.

Figure 3c shows the top view of a 200 μm radius pulley-coupled As₅Se₃ mid-IR microdisk resonator. The gap width between the disk and the single-mode bus waveguide is set to 2.75 μm to attain near critical coupling operation (Fig. 3d). Compared to the conventional coupler configuration, the pulley coupler design improves the fabrication tolerance by increasing the coupling strength[78]. Figure 4a shows the TE polarization transmission spectrum of the resonator. The group index calculated from the Free Spectral Range (experimentally measured FSR ~ 8.16 nm) is 2.63, which is close to our finite difference simulation result (2.68) assuming a fundamental transverse whispering gallery mode order (Fig. 3e) of the disk resonator. Loaded Q factors, measured from 22 resonant peaks in 3 different samples, range from $6 \times 10^4$ to $10^5$. Figure 4b shows the spectrum measured from the highest Q device near its resonance peak at 5157.9 nm wavelength. A loaded Q factor of $10^5$ was inferred from the spectrum, corresponding to an intrinsic Q factor of $2 \times 10^6$ and an equivalent waveguide propagation loss of 0.7 dB/cm. This Q factor is among the highest values reported in experimentally demonstrated mid-IR resonators.
Fig. 4. (a) Mid-IR optical transmission spectrum of the As$_2$Se$_3$ micro-disk resonator measured using a wavelength sweeping method; (b) spectrum near the optical resonance at 5157.89 nm wavelength (the red box in 4a). The dots are experimentally measured data and the line is the linear-scale Lorentzian fit, which indicates a loaded cavity quality factor of $10^5$.

3. CAVITY-ENHANCED MID-IR PHOTONIC SENSING

Fig. 5. (a) Mid-IR transmission spectrum of a 200 μm radius disk resonator in ethanol/cyclohexane solutions of different volume ratio (dots are measured transmission intensity, while line is peak fitting by lorentzian function). With increase of volume ratio, the quality factor and extinction ratio decrease along with resonance wavelength shift, (b) addition absorption induced by ethanol was linear fit as functions of ethanol volume ratio.

The high Q-factor and long optical path length in the ChG resonators make them ideal device platforms for mid-IR chemical sensing. Using ChG resonator devices fabricated following similar protocols [46], we further demonstrated on-chip mid-IR cavity enhanced chemical sensing capitalizing on the resonantly enhanced light-matter interactions in the resonator [79-81]. In the experiment, cyclohexane solutions containing different concentrations of ethanol was pipetted onto the resonator chip and the resonator transmission spectra were monitored in-situ. Cyclohexane was chosen as the solvent as it only exhibits a weak, flat absorption background in the wavelength range of interest (5.1 – 5.3 μm). On the other hand, ethanol has a weak (relative to its main IR absorption band at 3.9 μm which has an absorption coefficient of 2900 cm$^{-1}$) absorption peak centered around 5.2 μm wavelength. Figure 5a shows the resonator transmission spectra as the
device was immersed in cyclohexane solutions. The progressive decrease of extinction ratio with increasing ethanol concentration is a consequence of excess optical absorption induced by ethanol. Addition optical absorption induced by ethanol was obtained by subtracting the waveguide loss in pure cyclohexane from the total propagation loss when ethanol was present, and normalized by the modal confinement factor in the sensing region. The confinement factor is 0.10 based on our finite differential modal simulation for the waveguide we used in the experiments. Concentration-dependent optical absorption of ethanol at 5.2 μm wavelength was plotted in Fig. 5b. The absorption coefficient of ethanol in cyclohexane can be obtained by a linear fit of the plot to be $\alpha_{\text{ethanol}} = (74 \pm 3.4) \text{ cm}^{-1}$, which agrees well with measurement result ($\alpha_{\text{ethanol}} = 78 \text{ cm}^{-1}$) obtained on a bench-top FTIR spectrophotometer.

The detection limit of the cavity-enhanced sensing technique has been experimentally demonstrated to be less than 0.1 ng[82], mainly limited by optical propagation loss in the resonator. Further sensitivity enhancement requires using different sensing mechanisms such as photothermal spectroscopy[83-85] to boost the light-molecule interactions in the mid-IR.

4. MONOLITHIC INTEGRATION OF MID-IR WAVEGUIDE AND DETECTOR ON SILICON

Integration of active optoelectronic devices and passive photonic components are essential for realizing the “sensor-on-a-chip” platform. Chalcogenide compounds are uniquely poised for such active-passive integration given their compatibility with silicon monolithic integration. Here we present the fabrication and characterization of mid-IR waveguide-integrated PbTe detector monolithically integrated on silicon[86].

Fig. 6. (a) A schematic cross-sectional view of the integrated mid-IR detector (not to scale). (b) A schematic representation of the chip design. An MMI structure splits the light into two arms. The lower arm is used for alignment. The upper arm delivers light to the PbTe detector (blue region). Both arms adiabatically increase in width from 2 μm to 5 μm. The PbTe layer and Sn contacts lie underneath the waveguide. (c) A 45° view SEM image of the mid-IR device.
The device uses a 4 inch silicon wafer with a 3 \( \mu m \) thick thermal oxide layer as the starting substrate. All the thin films for device fabrication (PbTe, Sn, and Ge\(_2\)Sb\(_7\)S\(_{70}\) glass) are deposited by thermal evaporation used in previously reported protocols[50, 51]. A PbTe layer is deposited first, followed by a 300 nm thick Sn contact layer with the Ge\(_2\)Sb\(_7\)S\(_{70}\) (GeSbS) waveguide layer on top. We choose chalcogenide glass as the waveguide material given its superior chemical stability and compatibility with PbTe materials[56]. The structure of the waveguide-integrated detector chip is illustrated in Figure 6b. Light is first coupled into a 2 \( \mu m \) wide GeSbS waveguide. A multimode interferometer (MMI) structure splits the light into two arms that gradually increase to a 5 \( \mu m \) width to improve alignment tolerance between the PbTe layer and the waveguide. The upper arm delivers light into PbTe where most of the light is absorbed. The lower arm, without the PbTe layer, is used for alignment. Figure 6c shows the SEM image at 45° view.

![Responsiveivity of the integrated detector as a function of wavelength measured at room temperature.](image)

The PbTe absorption measurement is performed at room temperature. A tunable Cr\(^{2+}\):ZnS/Se laser (2.0–2.5 \( \mu m \), IPG Photonics) is first coupled to an aspheric lens (C037TME-D, Thorlabs) and then focused into the waveguide. Light from the waveguide output is collected by an IR camera for imaging as well as intensity measurement in the alignment arm. A source measurement unit (Keithley 2401 SMU) is connected to the metal contacts on the chip via two probes to measure the I–V curves. Optical power coupled into the detector is estimated by subtracting the power loss due to fiber/lens coupling from the total input laser power, and we calculated the responsivity to be about 1.0 A/W at 2250 nm wavelength. Wavelength-dependent responsivity from 2.1 \( \mu m \) to 2.5 \( \mu m \) wavelengths is plotted in Figure 7. Within our measurement error, the responsivity remains roughly constant throughout this range. The theoretical responsivity at 2250 nm, assuming unity absorption efficiency and unity photoconductive gain, is about 1.8 A/W. Our device therefore exhibits a photoconductive gain of 0.59 taking into account a simulated 94% optical absorption efficiency. This figure is consistent with the carrier lifetime and transit time estimated based on the device geometry and Hall carrier mobility. The Johnson noise spectral density calculated from the dark resistance of our device is \( 8.6 \times 10^{13} \) A/Hz\(^{1/2}\), which is much larger than the generation-recombination noise (about \( 10^{-19} \) A/Hz\(^{1/2}\) based on Hall effect measurements). Since current flowing through a photoconductor does not exhibit shot noise [87], Johnson noise limited detectivity of this device is therefore \( 2 \times 10^{12} \) Jones (cm·Hz\(^{1/2}\)/W). The results above demonstrate the viability of using polycrystalline PbTe materials for on-chip integrated mid-IR detection.
5. SUMMARY

In this paper, we presented the experimental demonstration of essential building blocks of mid-IR photonic circuits, including high-Q optical resonators as the sensing element and waveguide-integrated photodetectors as the light receiver. The use of amorphous and polycrystalline chalcogenide materials allows monolithic integration of these devices on a silicon platform and potentially facilitates integration with other components to ultimately enable the mid-IR “sensor-on-a-chip” platform.

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