Towards a low-cost on-chip mid-IR gas sensing solution: chemical synthesis of lead-salt photonic materials

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ABSTRACT

Mid-infrared (mid-IR) gas sensing technology has been widely received as a competitive choice for the newly emerging internet-of-things (IoTs) applications mainly due to its high sensitivity, selectivity and reliability. However, high cost and chip-integration challenges, on the contrary, still limits their potential development. Lead-salt materials are proposed to offer possible solutions to address these issues, and our previous works have demonstrated their outstanding photon generation and detection capabilities in the MIR region. In this work, towards the low-cost point, we demonstrate some preliminary experimental results for preparing lead-salt based high quality active MIR photonic materials. Using a modified oriented-attachment synthesis method, for the first time, PbSe films grown on amorphous glass substrates in the wet chemical process, presented a highly smooth surface having an uniformed crystal orientation in (111) direction. Further, their nanocrystal size can also be tailored to allow a broad range control of emission wavelength from 3.3 μm to 4.2μm owing to the unqiue quantum size effects. In conclusion, this new material growth exploration opens a possible cost-effective path to conduct active photonic waveguide engineering to manipulate light-and-matter interactions in the MIR range for potential chip-integrated sensing applications (e.g., IoTs).

Keywords: Mid-IR, Gas Sensing, Wet Chemical Growth, Lead Salts, Oriented Attachment, Quantum Effect

1. INTRODUCTION

The mid-infrared (MIR) spectral region covering wavelengths from 2 to 20 μm, contains fundamental molecule vibration signatures of almost all molecules[1] as well as two atmospheric transmission windows of 3-5 μm and 8-12 μm, and thus has a significant importance for a wide variety of sensing applications in medical diagnosis, environment protection, national security and defense, and industry process control fields. Various MIR sensing techniques,[2–5] have been explored through interacting light with molecules mainly based on the Beer-Lambert's law.[6] These kinds of sensing technologies have demonstrated very good stability, selectivity and sensitivity performance,[7] and therefore have been more and more commonly used in our lives nowadays.

With the emerging internet of things (IoTs) based new technology framework, there has been a global trend in devices[8] miniaturization for the integration with smartphones, tablets and wearable consumer electronics. Numerous efforts have been made in order to develop a transformative on-chip MIR sensor[9] in recent years. As a result, performance of active MIR light sources and photodetectors have been improved largely. Room temperature (RT) operating MIR laser sources (i.e., quantum cascade lasers (QCLs) and interband cascade lasers (ICLs))[10–13] have been successfully realized on III-V group semiconductor materials platform. In the wavelength range from 3 to 5 μm, the specific detectivity (D*) of MIR photodetectors has reached to 4×10^{12} Jones using IV-VI group lead-salt semiconductors.[14–16] For longer wavelength ranges, improvements on the miniaturization for pyroelectric and thermopile detectors have also contributed to the reduction of price and footprint.[17]

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However, those technology advancements still haven't been able to reach the complete on-chip integration of a practical MIR chemical sensor. Apparently, quantum engineered III-V MIR lasers offer incomparable performance and dominate light source markets for MIR sensing applications. But also because of that, cost and integration challenges have been preventing the sensor development progress. Both QCLs and ICLs are made of precisely controlled quantum-well and super-lattice structures, which require to use the expensive and time-consuming molecular beam epitaxy (MBE) ultra-high vacuum growth process. The room to reduce such cost is marginal. On the other hand, materials and substrates for low-cost non-cryogenic MIR photodetectors (PbSe, HgCdTe etc.) are different from the ones for QCLs/ICLs. Consequently, monolithic integration of key elements (laser, photodetector and gas cell) becomes almost impossible. From this point, it is important to explore alternative solutions to overcome those challenges.

We anticipate that lead salt materials could provide a possible new pathway for the on-chip gas sensor development. This group of direct narrow band semiconductors have high optical absorption coefficient and extremely low non-radiative Auger recombination rates.[18] By far, uncooled polycrystalline PbSe photoconductive detectors remain the major choice for MIR sensing applications operating in the 3-5 μm spectral range thanks to their high detection performance.[19] Besides, they have very good light emitting capabilities, especially at room temperature condition.[20,21] With these said, it is possible to fabricate both light source and photodetector on one substrate for monolithic integration purpose. In addition, lead salts also have highest refractive indices compared with other MIR material groups. This is an unique and outstanding property for confining light in active waveguides to manipulate light and matter interactions. Thus, besides the emitters and detectors, the lead-salt waveguide offers another key component for sampling gas molecules on chips. With all these factors being considered, it is very promising to develop sensing device in one chip based on lead-salt materials. Nevertheless, it is necessary to point out that, in order to conduct photonic design, the material morphology and geometry has to be well defined. However, polycrystalline lead salt materials prepared by the wet chemical process on amorphous substrates are generally with random crystal orientations and of very rough surface morphology comparable with the corresponding MIR wavelengths. To overcome this technical hurdle, in this work, we present our preliminary experimental exploration for preparing highly uniform and oriented lead-salt photonic nanocrystal films on glass substrates using a new hybrid wet chemical synthesis approach.

2. GROWTH METHOD AND EXPERIMENT DETAILS

Lead salts have various growth mechanisms in the chemical synthesis process.[22,23] Two of the most commonly reported and thoroughly investigated mechanisms that could lead to film-to-substrate deposition are the ion-by-ion growth and the cluster growth mechanisms. The ion-by-ion mode is a simple deposition process in which chemical reaction happens upon the substrate surface directly. This mechanism typically results in bulk films with irregular orientations. The cluster growth mode refers to a two-step process that solid clusters precipitate in solution and then diffuse to the substrate and assemble together into the nanocrystal forms. This mode could produce highly-dense and ultra-small quantum dot films.

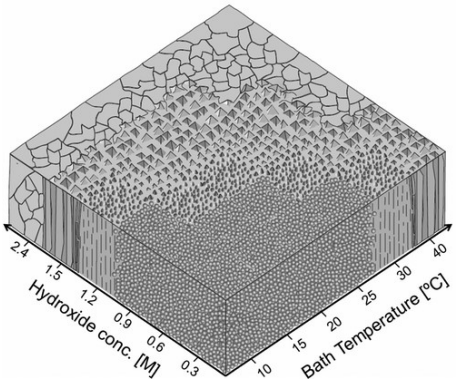

Figure 1. Structural zone model (SZM) for PbSe on GaAs(100) as a function of growth temperature and [OH–] concentration.[24]

T. Templeman etc.[24] recently reported a structural zone model (SZM), presented in Fig. 1, depicting an intermediate oriented attachment growth mechanism between ion-by-ion and cluster growth modes. This new mechanism can produce a highly uniformed (111) oriented PbSe microstructure films exhibiting low dimension quantum confinement effects covering a broad MIR wavelength range from bulk 4.2μm down to the near infrared (NIR) range. Such results are very encouraging. However, their novel growth can only be realized by using an epi-polished single crystal GaAs substrate.[25] When it comes to the photonic waveguide applications, high dielectric index GaAs substrate could cause a large optical leakage to affect the photonic performance negatively. Also, the high substrate cost is another concern. In view of their work, here, we refer their SZM as a basic guideline but further extend the understanding of the growth mechanism, and explore a modified wet-chemical approach leading to a similar oriented-attachment growth result but on amorphous glass substrates.

Materials and Chemicals used are listed as follows: Sodium sulfite (Aldrich, BioUltra, anhydrous, $\geq$98%), selenium powder (Aldrich, 100 mesh, 99.99%), lead (II) acetate trihydrate (Aldrich, $\geq$99.99%), and sodium hydroxide (pellets EMPLURA). a stock of sodium selenosulfate (Na_2SeSO_3), 0.2 M, was prepared by re-fluxing 0.2 M of selenium powder with 0.5 M of sodium sulfite. Glass slide substrates were thoroughly cleaned by soaking in solvent and RCA baths sequentially, and then washed in de-ionized water and purge-dried by N_2 gas. To prevent large precipitating particles from contaminating the growing film, the deposition side of the glass substrate was facing downwards, at an angle of about 70° with respect to the air–solution interface. The solution was prepared by diluting the lead acetate solution with water and adjusting the pH using sodium hydroxide in a range between 10-12. Finally, Na_2SeSO_3 was added to a 50 ml Pyrex beaker to initiate the growth.

The surface morphology of the as-grown thin films were characterized by using a Jeol JSM-6060 scanning electron microscopy (SEM) tool. Structural analysis were performed by using a Rigaku Ultima IV X-ray diffractometer (XRD) tool. The XRD data were collected over a 2θ range of 10° to 70° using Cu Kα radiation ($\lambda = 1.5405\mathring{A}$) at 40 kV. In materials' photo-luminescence (PL) measurement, a NIR diode laser operating at 980nm was used as the optical excitation source. The PL signals were then collected by a Bruker Invenio-R Fourier transform infrared Spectrometer using a high-gain cryogenic-cooled InSb photodetector. In addition, an amplitude lock-in approach was adopted in the PL measurement to suppress the background interference (e.g., ambient thermal radiation).

3. RESULTS AND DISCUSSION

To compare the morphology difference, three PbSe thin films were deposited on glass substrates using different wet chemical growth approaches. Their top-view SEM images are presented in fig. 2. In which, these samples have clearly shown very distinctive micro-structural formations.

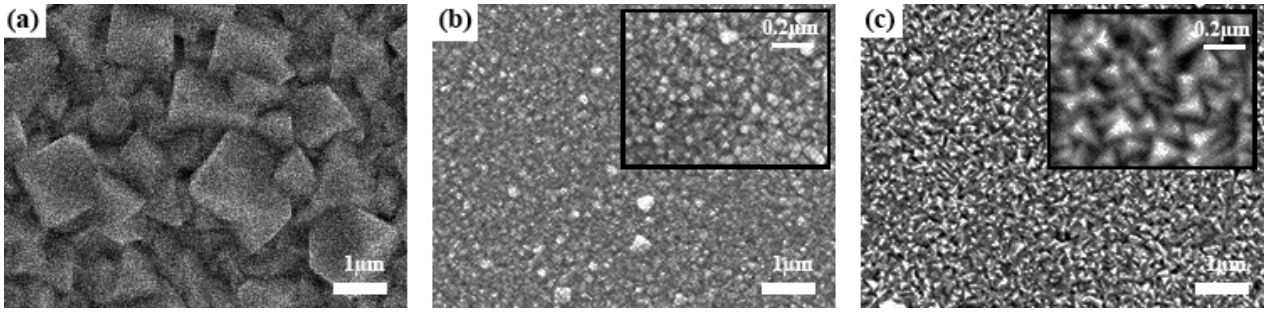

Figure 2. Top view SEM images of PbSe thin film samples prepared by a) a poly-crystalline high-temperature bath deposition; b) a low-temperature quantum dots deposition; b) modified oriented-attachment nanocrystal growth method. (note: the insets of (b) and (c) are $\times$5 zoom-in images of the corresponding samples.)

Fig. 2(a) presents a PbSe film prepared by the conventional chemical bath deposition method which is typically used for the fabrication of MIR photoconductive detectors. As shown, the film is composed of micro-scale cubic crystal grains with a random distribution of crystal orientations. This growth process was controlled under a high pH value (i.e., $\geq$12) and high temperature (i.e., $\geq$60°C) solution environment. As mentioned previously,

a high OH^{-1} concentration could slow down the formation of solid lead hydroxide nanocrystal clusters in the solution, and at the same time, a high growth temperature could activate the direct growth of PbSe nanocrystals on a glass substrate through the ion-by-ion mode. Because the substrate is an amorphous glass, there is no orientation selection related to the substrate which causes the random oriented morphology. Powder XRD measurement presented in fig. 3(a) also indicate that the PbSe film has multiple orientation indices in the cubic form. Additionally, it is noted that (200) is the strongest peak as opposed to others, which could be attributed to the lowest surface energy of PbSe's (100) crystal plane[26] that makes the (100) facets easier to attach to the substrate. Overall speaking, it has been pointed out that photonic waveguide design requires a much smaller material roughness as opposed to the targeted wavelength range. Because of that, although this approach may be suitable for detectors considering a large roughness could increase the lateral scattering and harvest more photons, it unfortunately cannot serve the purpose for creating photonic waveguides.

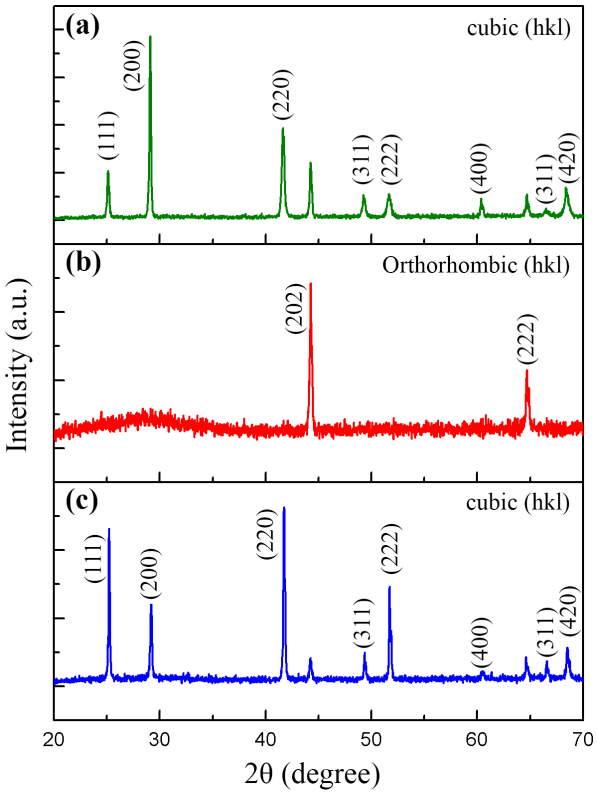

Figure 3. Powder X-ray diffraction diffractogram comparison of PbSe thin film samples prepared by a) a poly-crystalline high-temperature bath deposition; b) a low-temperature quantum dots deposition; b) modified oriented-attachment nanocrystal growth method.

Fig. 2(b), on the contrary, demonstrates a cluster-mode dominating procedure to grow the PbSe thin film on a glass substrate. The key parameter different from the first method is the growth temperature. While keeping the same pH concentration, in this new process, the growth temperature was controlled between 10 to 40 °C. Such a low temperature environment could hardly activate the ion-by-ion growth mechanism, and thus severely limits the direct cubic deposition on substrates. Consequently, the cluster mode played the major role leading to the deposition of a quantum dots stacking films on the glass substrate. XRD diffractogram in fig. 3(b) also can verify that cluster quantum structures are of orthorhomic form rather than the cubic nanocrystals. By referring the SEM image, it is clear that the surface roughness using this method can be reduced significantly down to a sub-50nm scale. From this point of view, the method may be good for the photonic design. However, PbSe quantum dots grown in such a low temperature environment are mostly in the early crystallization phase having ultra-small orthorhomic shapes. Their energy band gaps typically falls in the visible to the NIR range.

Therefore, it doesn't match with our photonic design intention in the MIR spectral range.

To some extent, these two approaches controlling either ion-by-ion or cluster growth mechanisms can both be generally described using the SZM model presented in Fig. 1. That said, intuitively, we then followed the oriented-attachment method suggested in Templeman's paper,[24] in which a transition growth zone was established between the ion-by-ion and cluster growth modes by providing a ultra-high OH^{-1} concentration with a moderately low bath temperature. This special synthesizing zone had successfully enabled the oriented growth of PbSe nanocrystals on epi-ready GaAs (100) substrates. However, in our attempts, by changing the substrate to others (e.g., glass or silicon wafers), we found that the growth mechanism has failed to be activated. The substrates after the growth still remained almost clear, barely having any film deposited but only a few cubic PbSe crystals scattered on. Such a different phenomenon can not be explained by their SZM model. To understand the reason, our suggested explanation is that epi-ready GaAs substrates offer an unique and critically important high-density crystal seeding layer that could reduce the activation threshold of the oriented-attachment mode to a low temperature transition region between ion-by-ion and cluster dominating zones. However, when it comes to other hetero-substrates such as glass or Si wafers, this special activation layer is missing thus can not lead to the oriented-attachment growth results.

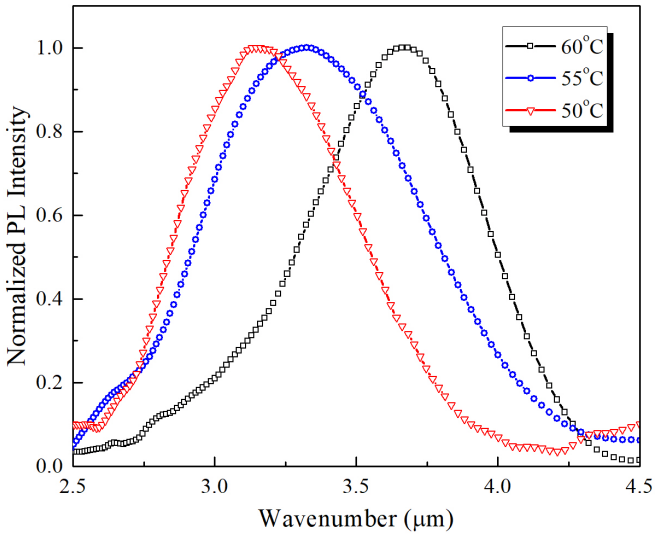

Figure 4. The photo-luminescence (PL) emission spectra from PbSe films prepared by the modified oriented attachment method at varying deposition bath temperatures.

With this new theoretical understanding, we developed a modified oriented-attachment growth procedure that doesn't involve the use of crystalline GaAs (100) substrate. An additional step was used to form a similar seeding layer using a intermediate solution treatment process. In this step, the wafer was wet-coated with an atomic-scale thin PbSe layer in a high temperature but a low pH value (i.e., 10-11) environment. The general guideline is to promote the growth transition from cluster dots to cubic crystal grains. After that, the condition will be adjusted to the one described by the standard oriented-attachment method.[24] It is found that such a hybrid procedure can effectively reproduce the oriented growth result without the use of GaAs wafers. Further in-depth discussion of this additional wet-chemical step for preparing the seeding layer will be presented in future after a systematical experimental investigation.[27] Here we mainly focuses on reporting the newly explored preliminary growth results. As shown in the top-view SEM image in fig. 2(c), by applying this modified chemical approach, a similar highly uniformed PbSe (111) oriented nanocrystal thin film layer can been successfully created directly on a amorphous glass substrate. Pyramidal tip arrays are revealed clearly in the inset of 3(c). At the same time, XRD characterization indicates that {111} group oriented crystal gains dominates in the film compared with the {100} group. The (220) peak is considered to result from the tilted pyramidal crystals. This angle randomness is suggested to be attributed to the missing of crystalline substrates. It is emphasized that although the oriented attachment mode dominates, other mechanisms still exist and may lead to the growth of surface contaminant.

So 200 group of peaks are considered to be from some scattered large crystal contamination due to the minor ion-by-ion process. Lastly, thanks to the large Bohr radius of lead salt semiconductors[28] (i.e., PbSe 46nm, PbTe 46nm and PbS 20nm), quantum confinement effects can be achieved in the MIR spectrum range by controlling PbSe's cubic crystal gain sizes. To demonstrate the quantum effect, the direct bandgap radiative emission of PbSe films was measured using PL as a function of gain size of the pyramidal crystal gains. The preliminary results are presented in 4. A clear transition toward higher band gap energies can be seen by reducing the bath temperature from 60 to 50°C. It is worth noting that the the ability to tuning the PL emission of the PbSe material in this wavelength range is of special importance since many important gas molecules such as hydrogen sulfide (H_2S), hydrocarbon group (e.g., CH_4, C_2H_5 etc.) all have strong absorption peaks in between 3-4 μm.

4. CONCLUSIONS

In summary, in this paper, we reported a preliminary experimental work to synthesize an oriented PbSe nanocrystal film using a new modified oriented-attachment method. Both the high temperature chemical bath deposition method and low temperature cluster growth method are firstly presented to proven their ineligibility for the photonic waveguide design in the MIR region. Then, the PbSe film prepared by new orentied attachment process are presented which offers a highly-smooth top surface with roughness smaller than 100 nm. Besides, it is composed of (111)-oriented PbSe nanocrystal gains whose crystal size can be manipulated to deliver size-dependent quantum confinement effect in MIR wavelength domain. Last but not least, the film can be directly deposited on any low refractive index substrates. These unique properties offers several new dimensions of design freedoms thus make this film an ideal choice for conducting the photonic waveguide engineering to investigate light-matter interactions in the MIR spectrum.

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