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PAPER

A novel quaternary alloy (Cu2Zn1−xCd,xSnS4) nanostructured sensor for biomedical diagnosis

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Abstract

A new quaternary alloy (Cu2Zn1−xCd,xSnS4) nanostructure with different proportions of cadmium (Cd) was synthesised using spin coating technique on oxidized silicon (100) substrate and analysed by x-ray diffraction (XRD) and photoluminescence (PL). The XRD peaks were shifted towards the lower angle side with increasing Cd concentrations. A shift of PL band gap from 1.79 eV (x = 0) to 1.69 eV (x = 1) was observed. We attributed this phenomenon to the phase transition from kesterite to stannite phase in the series of Cu2Zn1−xCd,xSnS4 (0 ≤ x ≤ 1) quaternary alloy nanostructures. Further, the generated novel structure was found to be more suitable for biomedical diagnosis, as evidenced by dengue serotype-2 detection with higher specificity. The biosensor shown with quaternary alloy nanostructure could attain the sensitivity to 100 fM and able to discriminate specific DNA from dengue against single and triple mis-match sequences. The biosensor demonstrated here with a novel Cu2Zn1−xCd,xSnS4 quaternary alloy nanostructure opens the way for developing high-performance biosensors.

Introduction

Significant attention has been paid to the CuIn1−xGa,xSe2 (CIGS) film for its high power conversion efficiency and stability [1–3]. Nevertheless, the high costs of gallium and indium obstruct the further development of CIGS [4]. Due to its direct band gap (Eg ~ 1.5 eV) as well as high absorption coefficient (>10⁴ cm⁻¹), Cu2ZnSnS4 (CZTS) is considered as a potential material to substitute CIGS, and it has attracted great interest earth-abundant elements [5–8] and the highest reported efficiency of CZTS solar cell is 10.6% [9].

It was reported that high concentrations of acceptor Cu2Zn antisites and Cu vacancies could be determined intrinsic p-type conductivity of CZTS. Therefore, the fact that the ionic radius of Cu and Zn is about the same [10], the possibility of formation of undesirable ZnCu antisite defects in CZTS is increased. Moreover, the ZnCu defect will have a significant adverse effect on the electrical properties of CZTS [10]. However, CdCu defects will not be easily formed in the case of Cu2+ Cd2+ Sn4+ S4− (CCTS), because the ionic radius of Cd2+ ions is greater than that of Cu+ ions. Other experimental studies [11–13] have showed that CCTS also possesses a large absorption coefficient (>10⁵ cm⁻¹) and a promising band gap (1.37 eV) analogous to CZTS.

The tuning of CZTSSe band gap through substitution of Sn by Ge or Zn by Cd atoms in the crystal lattice forming new Cu2ZnGeSe4 or Cu2CdSnS4 in the monograin powder form has been done [14]. The phase composition of synthesized powders was determined by x-ray diffraction (XRD) and Raman spectroscopy. The effective energy band gaps determined from the quantum efficiency (QE) data of the Cu2ZnGeSe4 and Cu2CdSnS4 devices are 1.35 and 1.4 eV, respectively. Dispersible quaternary nanocrystals were successfully prepared [15] by a toluene-thermal and a hot-injection approach and characterized using UV–vis spectroscopy, x-ray powder diffraction (XRD), and transmission electron microscopy (TEM). By referring to Chen et al [16] who have emerged the dawn of a new era in optoelectronic technologies with the recent development of the organic–inorganic hybrid halide perovskite. Its exceptional attributes, including high carrier mobility, an adjustable spectral absorption range, long diffusion lengths, and the simplicity and affordability of fabrication
render it one of the most exceptional and market-competitive optoelectronic materials for applications in photovoltaics, light emitting diodes (LED), photodetectors, lasers, and more for various practical.

Variety of techniques has been reported for the deposition of CZTS like hydrazine deposition [17], sputtering [18], spray pyrolysis [19], PLD [20] thermal co-evaporation [21], and solvothermal [22]. In the current work, the sol–gel method was used for the preparation of a novel Cu2Zn1−xCdxSnS4 quaternary alloy nanostructure with different Cd concentrations (x = 0, 0.2, 0.4, 0.6, 0.8, 1) on oxidized silicon substrate, this method is a very simple and cost-effective without involving vacuum system. Further, Cu2Zn1−xCdxSnS4 quaternary alloy nanostructures is characterized, and how the stacking order of the precursor films affects the structural and optical properties of the resultant CZCTS nanostructures. The novelty of Cu2Zn1−xCdxSnS4 quaternary alloy nanostructure was evidenced by demonstrating for biomedical diagnosis with the detection of DNA sequence from dengue serotype-2, the obtained results displayed high-performance of Cu2Zn1−xCdxSnS4 quaternary alloy nanostructure to be used as a biosensor.

**Experimental procedure**

**Preparation of SiO2**

A p-type silicon wafer was cleaned using standard RCA1, RCA2 cleaning solutions to remove organic and inorganic contaminants and the native oxide layer on the wafer surface. Next, the silicon wafer was rinsed and cleaned with deionized water. SiO2 layer with approximately 200 nm thick was produced on the cleaned wafer surface using a wet oxidation furnace. Using a conventional lithography process, an interdigitated electrode (IDE) device of 7 × 5 mm in size was patterned using negative resists (NR7-6000PY) on the SiO2/Si substrate.

**Fabrication and characteristics**

The aged Cu2Zn1−xCdxSnS4 quaternary alloy nanostructure was deposited onto oxidized silicon substrate using a spin coating technique. First solution of Cu2Zn1−xCdxSnS4 precursors was prepared from copper (II) chloride dehydrate (0.3 M), zinc (II) chloride dehydrate (0.3 M), tin (II) chloride dehydrate, cadmium (II) chloride (0.3 M), thiourea (0.6), 2-methoxyethanol (2-metho) and monoethanolamine (MEA). The 2-metho and MEA were used as solvent and stabilizer, respectively. The mole ratios of Cu (Zn + Cd), Sn, and S in the solution are 2:1:1:4. In order to obtain the solution with different Cd concentrations (x), the mole ratios of Cd to Zn + Cd in the solution vary according to the value of x as 0, 0.2, 0.4, 0.6, 0.8 and 1. In order to completely dissolve the metal compounds during stirring the milk solution became a yellow, the solution was stirred at 50 °C for x h to keep the deposited nanostructures coherent, and then, the samples were cooled to below 40 °C in the chamber. The coating and drying processes were repeated for seven times to obtain ≈1 μm thickness. After that, Ag metal contacts were formed on Cu2Zn1−xCdxSnS4 quaternary alloy nanostructures with Cd concentration equals 0.6 deposited onto oxidized silicon substrate using PVD-HANDY/2STE (Vaksis Company) vacuum thermal evaporation in the pressure of 4.5 × 10⁻⁵ Torr and the contacts were formed in the form of zig-zag with length of 5 mm and 100 nm thicknesses. The contact area of the diode was found to be 3.14 × 10⁻⁵ cm².

X-ray diffraction (XRD) system (Philips PW 1710 x-ray diffractometer) with Cu Kα radiation (λ = 1.54 Å) was utilized to examine the crystal structure of Cu2Zn1−xCdxSnS4 quaternary alloy nanostructures with x = 0, 0.2, 0.4, 0.6, 0.8, 1. XRD patterns were recorded in the range of 30° to 70° operating at a voltage of 40 kV and a current of 40 mA. Photoluminescence (PL) spectroscopy system (Jobin Yvon model HR 800 UV system) was applied at room temperature using He-Cd laser (λ = 325 nm). Surface morphologies and measurement of the grain size were investigated by field emission-scanning electron microscope (FE-SEM) system (NOVA NANO SEM 450).

**DNA immobilization**

To demonstrate the biosensing application of Cu2Zn0.4Cd0.6SnS4 quaternary alloy nanostructure, we designed specific DNA oligonucleotides from dengue serotype-2. Totally, 5 different oligonucleotides were prepared, which include capture probe, specific target, single mis-matched and triple-mismatched and complementary sequences. The sequence of dengue serotype-2 specific capture DNA probe modified with carboxylic group at 5’-end and it consists; 5’-COOH-ATGAAGCTGTAGTCTCACTGGAAGG-3’; the target sequence is 5’CCTTCCAGTGAGACTACAGCTTCAT3’; the single mis-matched target sequence is 5’CCTTCCAGTGAGACTACAGCTTCAT3’; the triple mis-matched target sequence is 5’CCTTCCAGTGAGACTACAGCTTCAT3’; the complementary sequence is 5’-ATGAAGCTGTAGTCTCACTGGAAGG-3’ [23].
To immobilize the capture probe (5'-COOH-ATGAAGCTGTAGTCTCACTGGAAGG-3'), after thoroughly cleaned the surface modified with 3-(Triethoxysilyl)propyl-1-amine (3APT) on Cu2Zn0.4Cd0.6SnS4 quinternary alloy nanostructure. Then using N-hydroxysuccinimide (NHS) and N-ethyl-N’-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC), the surface was activated to capture the probe. After thorough washing, 1 μM of capture DNA probe was immobilized and analysed against specific and non-specific DNA probes. The free surface after attaching the capture probe was blocked with 1 M Ethanolamine. To determine the sensitivity level of the specific target DNA sequence, probe captured was titrated with different concentrations, 100 fm, 1 pm, 10 pm, 100 pm, 1 nM and 10 nM. Dielectrical measurements of current to voltage (I–V) were taken using a Keithly 2400 source meter, USA. The reading was recorded from –6 V to 6 V.

Results and discussion

A novel quinternary alloy (Cu2Zn1−xCdxSnS4) nanostructured sensor for biomedical diagnosis is demonstrated in this study. The crystallized Cu2Zn1−xCdxSnS4 quinternary alloy nanostructure has the same CIGS properties. This stable quinternary compound crystallizes in the kesterite form with a tetragonal structure, and can be considered as an ordered cubic II–VI lattice derivative. The most important characteristic of this membrane is not necessary to be equal membrane components, because the copper atoms sit on the sites of zinc atoms and makes connectivity (p-type). On this structure, detection of dengue serotype-2 was desired as it is prevalent type found in the past. The genome position chosen for dengue serotype-2 DNA was from 10 557–10 581 (GenBank accession number: M20558).

Figure 1 shows the XRD patterns of Cu2Zn1−xCdxSnS4 quinternary alloy nanostructures with different concentrations; x = 0, 0.2, 0.4, 0.6, 0.8 and 1. The major diffraction peaks were indexed as corresponding to (112), (200) and (220) planes of kesterite phase of Cu2ZnSnS4 (ICDD PDF2008, 01-075-4122) and stannite phase of Cu2CdSnS4 (ICDD (PDF2008), 00-029-0537). Figure 1 shows the enlarged view of the (112) diffraction peaks. The XRD peaks were shifted towards the lower angle side with increasing Cd concentration indicating that the lattice constant increases. The expansion of lattice constant is attributed to Cd ion radius that is larger than Zn. The Cd atom has 1.53 Å larger than Zn atom (1.33 Å) also indicating that Cd mostly substitutes for Zn. The lattice constants a and c in (Å) were found to be 5.43, 10.81; 5.44, 10.82; 5.45, 10.85; 5.53, 10.98; 5.56, 11.27; 5.57, 11.32 using Bragg’s equation [24] in agreement with experimental data [25–27] from XRD data correspond to (112) plane. Followed by measured particle size 34.55, 35.76, 36.25, 48.44, 59.89, 63.30 using Scherrer’s formula [24] for different Cd concentrations, respectively.

The morphology of Cu2Zn1−xCdxSnS4 quinternary alloy nanostructures was investigated using FE-SEM. Figure 2 illustrates the FE-SEM images of as-deposited Cu2Zn1−xCdxSnS4 quinternary alloy nanostructures with different Cd concentrations. It can be seen further in figures 2(a)–(c) that the surface exhibits a homogeneous morphology over the whole SiO2 substrate, as demonstrated by the lack of holes or cracks. While, figures 2(d)–(f) displays smooth morphology, as well as the improvement in grain size. The increasing of grain size could be clearly seen with different Cd concentrations. The as deposited CZCTS quinternary alloy nanostructure yields a rounded, granular nanostructure with few cracks at x = 1.

The grain size increasing is shown with increasing Cd concentrations, which indicates an increase of film crystallinity. The measured grain sizes are as the followings: 27.06 nm for Cu2ZnSnS4, 29.23 nm for Cu2Zn0.8Cd0.2SnS4, 34.27 nm for Cu2Zn0.6Cd0.4SnS4, 39.6 nm for Cu2Zn0.4Cd0.6SnS4, 65.64 nm for Cu2Zn0.2Cd0.8SnS4 and 68.18 nm for Cu2CdSnS4 nanostructures.

The aforementioned sizes show an increasing as Cd concentration increases. It is important to understand that the aspect ratio of the nanostructures increases from 27.06 to 68.18 nm in going from Cu2ZnSnS4 to Cu2CdSnS4 (figure 2). This phenomenon can be explained as: the enhanced reactivity of Cd compared to Zn with the 2-methoxyethanol results in more rapid nuclei formation and subsequent kinetics-driven growth. Although a small difference of size is detected using Scherrer’s formula and FE-SEM, both have the same trends. It is a common phenomenon that efficiency of polycrystalline improves with increasing grain size of absorber layer; therefore, larger grains are required for improving the device efficiency.

PL spectra of CZCTS quinternary alloy nanostructures with different Cd concentrations measured at room temperature are showed in figure 3. PL spectra consist of one broad asymmetric PL band at 1.76 eV in Cu2ZnSnS4 and at 1.69 eV in Cu2CdSnS4. A shift of the PL band of Cu2Zn1−xCdxSnS4 quinternary alloy nanostructures towards highest wavelengths with increasing Cd concentration is observed in the region 0 ≤ x ≤ 1. This shifting is due to the substitution of Zn atoms with Cd atoms to produce a lower energy gap [28, 29].

The selectivity of the DNA biosensor was studied using the Ag/Cu2Zn0.4Cd0.6SnS4/SiO2/Si electrode (figure 3(a)). With the above obtained Cu2Zn0.4Cd0.6SnS4 quinternary alloy nanostructure, we have demonstrated it for biosensing medical applications as shown with other biosensors [30–36]. As discussed above...
a specific DNA sequence from dengue serotype-2 was chosen and evaluated with specific and non-specific DNA sequences. For specific DNA duplex formation after immobilized the capture DNA probe (5’- COOH-ATGAAGCTGTAGTCTCACTGGAAGG-3’), different concentrations of specific DNA sequence (5’CCTTCCAGTGAGACTACAGCTTCAT 3’) was titrated from 100 fM to 10 nM. For measuring the changes with DNA duplex formation, we used impedance spectroscopy. With this titration, we could notice the changes in the dielectric properties upon duplex formation, further these changes were in concentration dependent manner. The obtained results were clearly indicate, in the presence of Cu$_2$Zn$_{0.4}$Cd$_{0.6}$SnS$_4$ quinernary alloy

![Figure 1. XRD patterns of Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ quinernary alloy nanostructures with different Cd concentrations (x = 0 to 1). Respective peaks were indicated by coloured spheres.](image)
nanostructure, we could attain the sensitivity down to 100 fM (calculated based on 3σ method), as it showed more than 3 fold higher dielectrical changes compared to the control sample (figure 4(b)).

For specificity analyses, we used three types of sequences, which include the single mis-match (5’ CCTTCCAGTGTGACTACAGCTTCAT 3’), the triple mis-match (5’ CCTTCCAGTGTCTCTACAGCTTCAT 3’) and the complementary (5’ - ATGAAGCTGTAGTCTCACTGGAAGG-3’) sequences. We could see clear difference between specific against single and triple mis-matches, whereas the complementary sequence does not show any significant changes with the dielectric property (figure 4(c)). Further, the designed sensor has prolonged stability, as we could regenerate the sensing surface with boiled water (to remove target from probe) and reuse.
Figure 4. (a) Illustration for fabrication of Cu2Zn0.4Cd0.6SnS4 quaternary alloy nanostructure. (b) Dielectric measurements with DNA duplex formations with the sequences of dengue serotype-2 using concentration dependent electrical changes. Measured from 100 fM to 10 nM. (c) Specificity assay with complementary, single and triple mis-matching sequences.
Conclusions

In summary, stable solid solutions of Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ (x = 0, 0.2, 0.4, 0.6, 0.8 and 1) quaternary alloy nanostructures were synthesised using spin coating technique on oxidized silicon (100) substrate. The analysis of novel Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ quaternary alloy nanostructure with different concentrations allowed determining the dependence of PL band position and energy band gap of absorber on the nanostructures composition. The obtained results showed that incorporation of Cd into the CZTS causes decreasing of energy gap values from 1.79 to 1.67 eV. Structural studies indicated that the phase transition from kesterite to stannite occurs around x = 0.6. As a proof, this Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ quaternary alloy nanostructure to be a nanobiosensor, we demonstrated with the detection of dengue serotype-2 using DNA duplex strategy and attained the sensitivity to 100 fM, proved as a model DNA sensor.

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