Epitaxial Synthesis, Band Offset, and Photoelectrochemical Properties of Cubic Ga₂S₃ Thin Films on GaAs (111) Substrates

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Uniform and crack-free cubic Ga₂S₃ thin films have been epitaxially synthesized on n-GaAs (111) substrates by sulfurization. Atomic-force microscopy revealed that the Ga₂S₃ surface is dominated by nanoparticles of smaller than 50 nm in diameter. The nanoparticles, clustered into regular triangle structures that hierarchically packaged on GaAs, significantly reduced the reflectance of GaAs. Low-temperature photoluminescence revealed typical acceptor-like defects while X-ray photoemission spectroscopy revealed type-I heterojunction with a valence-band offset of 0.6 eV for the Ga₂S₃/GaAs heterostructure. Photoelectrochemical properties of the Ga₂S₃/n-GaAs (111) heterojunction are studied and compared with those of bare n-GaAs (111) substrate in a typical three-electrode setup.

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Because of their optimal band gaps (1.1 to 1.7 eV) for efficient solar driven water splitting, conventional semiconductors, including Si, GaAs, and GaP, have shown great promise in the direct photolysis of water to generate hydrogen fuel using sunlight. Unfortunately, these semiconductors are generally unstable—either being corroded or passivated—when working as a photoanode in aqueous electrolytes. Coating of metals and/or transparent metal oxides could somehow stabilize the semiconductor photoanode during water oxidation. Hu et al. recently reported that a thin amorphous TiO₂ layer of 4 to 143 nm in thickness coated on Si or GaAs by atomic layer deposition can effectively prevent their photocorrosion. This TiO₂ coating, together with a layer of patterned Ni islands, stabilized the semiconductor photoanodes and promoted their efficiency for water oxidation. Here, the benefit of TiO₂ coating is twofold, one is its larger bandgap than that of the semiconductors, so that the light absorption of the semiconductors is not much affected. The other is its electronic defects, which promote the electrical conduction of holes.

Gallium sulphide has long been of interest as a surface passivation material for GaAs. Recent studies revealed that Ga₂S₃ is highly resistive to light irradiation. Intrinsically, Ga₂S₃ is rather hole conductive because the Ga sublattice of Ga₂S₃ is 1/3 unoccupied (i.e., Ga vacancies) which forms electron traps located at ~0.4–0.7 eV above the valence-band maximum (VBM). These characteristics of Ga₂S₃ as well as its large bandgap (>3.0 eV) are basically common with those of TiO₂ when coated on GaAs photoanode as mentioned above. Recently, we reported a simple and low-cost material growth method that yields Ga₂S₃ crystals on epitaxially n-type GaAs (111) substrates. However, the crystal phase of the Ga₂S₃ layer varied from cubic to monoclinic and/or hexagonal along the growth direction; onset of film cracking and lift-off also occurred due to the large film thickness (~450 nm).

In this work, thinner Ga₂S₃ layers were prepared in a tube-furnace setup. The detailed growth procedure for Ga₂S₃ can be found in Ref. 8, the only variations here are the reduced growth temperature and time, i.e., from 650 °C and 20 min to 600 °C and 10 min, respectively. The structural and optical properties of the Ga₂S₃ were characterized using atomic-force microscopy (AFM), high-resolution X-ray diffraction (HRXRD), X-ray photoelectron spectroscopy (XPS). Photoelectrochemical properties of the Ga₂S₃ coated n-GaAs were studied with a typical three-electrode setup consisting of a Pt-foil as the counter electrode, Ag/AgCl as the reference electrode, and Ga₂S₃/n-GaAs as the working electrode; 0.1 M Na₂SO₄ was used as the electrolyte. A solar simulator setting at AM1.5 (100 mW/cm²) was used as the light source for the illumination. A 1.0 V bias was applied across the coated film and the Pt electrode. A solar simulator, adjusted to a power density of 50 mW/cm², was used as the light source. The amount of gas evolved was determined through a gas chromatograph.

The image shown in Fig. 1a is taken by a nomarski microscope, which shows a uniform and crack-free surface of the obtained Ga₂S₃ layer. The microstructure of the Ga₂S₃ surface recorded by AFM is shown in Fig. 1b, where one sees that nanoparticles of smaller than 50 nm in diameter clustered into submicron regular triangle structures that hierarchically packaged on the GaAs substrate. The in-plane orientation of the individual triangle structures more or less aligned with one another. Optical spectroscopy studies (spectra not shown for the sake of brevity) revealed that the surface reflectance of the Ga₂S₃ (111) substrate is significantly reduced by such a Ga₂S₃ coating, especially in the wavelength range from ultraviolet to visible. A typical cross-sectional scanning-electron microscopic (SEM) image is shown in Fig. 1c, from which the thickness of the Ga₂S₃ layer (i.e., 150 nm) is clearly determined. It is also seen that the Ga₂S₃ layer is uniform in thickness and the heterostructure has a sharp interface as indicated by the arrow.

Figure 2a shows the HRXRD θ/2θ-scan pattern collected from the Ga₂S₃/GaAs heterostructure around the (111) atomic planes, which, together with the θ-scan patterns collected from the (220) atomic planes in Fig. 2b, provides clear-cut evidence that the Ga₂S₃ is cubic phase and epitaxially grown on the GaAs substrate with the epitaxial relationship of [110]Ga₂S₃(111)//[110]GaAs(111). This epitaxial relationship, typically the 3-fold in-plane rotation symmetry [Fig. 2b], is consistent with the collective in-plane orientation of the triangle structures in Fig. 1b. Figure 2c shows a reciprocal space mapping (RSM) collected around the (220) atomic planes of both the Ga₂S₃ epilayer and the GaAs substrate. The RSM was collected in a skew configuration, so that the alignment between the Ga₂S₃ (220) and GaAs (220) diffraction peaks in Q₁ does not necessarily imply the absence of strain relaxation in the Ga₂S₃ epilayer. In fact, a careful calculation of the lattice spaces from Figs. 2a and 2c, using q̃GaAs = 0.5653 nm as the reference, revealed q₁₁₁ = 0.3005 nm and q₁2₂₀ = 0.1840 nm for the Ga₂S₃ epilayer. These results, when assuming Ga₂S₃ = 0.5215 nm (JCPDS-ICDD 43-916), correspond to lattice strains of ε₁₁₁ = −0.30% and ε₁2₂₀ = −0.28% remaining in the Ga₂S₃ epilayer. The relatively small lattice strains and the almost same strain in the (111) and (220) directions provide evidence that the Ga₂S₃...
Ga$_2$S$_3$/GaAs heterostructure at 10 K using a 532-nm laser excitation. The spectrum in Fig. 3a exhibits two dominant features corresponding to the near-bandedge emission (NBE) and a deep-level emission (DLE) of GaAs located at about 1.48 and 1.21 eV, respectively. This is because the excitation energy (NBE) and a deep-level emission (DLE) of GaAs located at about two dominant features corresponding to the near-bandedge emission of P1 and P2 when the sample temperature is varied, most likely due to the varied excitations of the Ga vacancies. The NBE feature due to the varied excitations of the Ga vacancies. The NBE feature [i.e., P1 in Fig. 3b] indicates that the bandgap energy of the cubic Ga$_2$S$_3$ is $\sim$3.2 eV. This value is slightly larger than that obtained by optical absorption spectroscopy (3.0 eV) but closer to that obtained by PL (3.4 eV) in the literature.8,15–17

To verify the difference of $\Delta E_V$ in Eq. 1, a thin layer of Ga$_2$S$_3$ ($<$10 nm) was prepared on an n-GaAs (111) substrate so that the XPS signals can be detected from both the Ga$_2$S$_3$ layer (i.e., S$_2p$) and the GaAs substrate (i.e., As$_3d$). Figures 5a–5c show the XPS spectra collected from a thick (150 nm) and a thin ($<$10 nm) Ga$_2$S$_3$-coated n-GaAs (111) heterostructures and a bare n-GaAs (111) substrate, respectively. Besides the typical VB and the core levels of S$_2p$ and As$_3d$ in Figs. 5b and 5c determine P$_3$ is much faster than those of P$_1$ and P$_2$. These comparisons indicate that there is a competition between the recombinations channels of P$_1$/P$_2$ and P$_1$ when the sample temperature is varied, most likely due to the varied excitations of the Ga vacancies. The NBE feature of Ga$_2$S$_3$ [i.e., P1 in Fig. 3b] indicates that the bandgap energy of the cubic Ga$_2$S$_3$ is $\sim$3.2 eV. This value is slightly larger than that obtained by optical absorption spectroscopy (3.0 eV) but closer to that obtained by PL (3.4 eV) in the literature.8,15–17

To our knowledge, the band offset of Ga$_2$S$_3$/GaAs heterostructures is lacking in the literature. Most of the reported studies on Ga$_2$S$_3$ were focused on bulk crystals for optical/optoelectronic applications and surface passivation of GaAs.16–20 The former cases have nothing to do at all with the band offset while in the later cases the Ga$_2$S$_3$ layers are usually too thin (i.e., a few monolayers) for the band offset measurement. In this work, cubic Ga$_2$S$_3$ thin layers with quite good structural and optical properties have been epitaxially grown on GaAs (111) substrates. In this light, the VB offset of the Ga$_2$S$_3$/GaAs (111) heterostructure can be measured by XPS according to the band diagram shown in Fig. 4, where, the valence- and conduction-band offsets read

$$\Delta E_V = (E_{GaAs}^{V_{3d}} - E_{Ga}^{V_{3d}}) - (E_{Ga}^{S_{2p}} - E_{Ga}^{S_{2p}})$$
$$\Delta E_C = E_{Ga}^{S_{2p}} - E_{Ga}^{As_{3d}} - \Delta E_C$$

To verify the difference of $E_{Ga_{As_{3d}}}^{V_{3d}} - E_{Ga_{As_{3d}}}^{V_{3d}}$ in Eq. 1, a thin layer of Ga$_2$S$_3$ (<10 nm) was prepared on an n-GaAs (111) substrate so that the XPS signals can be detected from both the Ga$_2$S$_3$ layer (i.e., S$_2p$) and the GaAs substrate (i.e., As$_3d$).
Figure 3. (a) PL spectrum collected at 10 K from the Ga$_2$S$_3$/GaAs (111) heterostructure using a 532-nm laser excitation, (b) temperature-dependent PL spectra collected from the Ga$_2$S$_3$/GaAs (111) heterostructure at 10–180 K using a 325-nm laser excitation. The asterisks indicate the emissions from GaAs.

Figure 4. Schematic energy band diagram for the Ga$_2$S$_3$/GaAs heterostructure.

Figure 5. XPS spectra for the valence-band offset measurement of the Ga$_2$S$_3$/GaAs (111) heterostructure: (a) S2p and valence-band (VB) spectra of a thick (~150 nm) Ga$_2$S$_3$-on-GaAs (111) sample, (b) S2p and As3d spectra of a thin (~10 nm) Ga$_2$S$_3$-on-GaAs (111) sample, and (c) As3d and VB spectra of a bare GaAs (111) substrate.

Figure 6. Linear sweep voltammograms of the 150-nm Ga$_2$S$_3$-coated n-GaAs (111) photoanode in 0.1 M Na$_2$SO$_4$ electrolyte measured under dark and AM1.5 illuminations. For comparison, a bare n-GaAs (111) substrate is also measured under the same conditions and the results are presented in Fig. 6b. It is clearly seen that not only the photocurrent but also the dark current are significantly increased by the Ga$_2$S$_3$ coating. Based on the structural properties of the Ga$_2$S$_3$ coating discussed earlier, we believe that the increase in photocurrent is mainly caused by the reduced surface reflectance while the increase in dark current is due to the roughened surface that increased the effective surface reaction area (see later discussion). Also seen in Figs. 6a–6b is that the onset of the increase in the photocurrents is lowered from the potential of 0 to −0.45 V versus Ag/AgCl by the Ga$_2$S$_3$ coating. This potential lowering is reasonable since the VB offset of the Ga$_2$S$_3$/GaAs (111) heterostructure, as measured by XPS, is 0.6 eV.

Figure 7. Hydrogen evolution reaction at the Pt counter electrode is further analysed. Figure 7a shows the H$_2$ evolution with Ga$_2$S$_3$/n-GaAs (111) as the photoanode, which was immersed in 0.1 M Na$_2$SO$_4$ electrolyte biased at 1.0 V versus Ag/AgCl, and under an illumination of 50 mW/cm$^2$. Evolved H$_2$ gas was clearly detected after about a 1-hour reaction and the gas production [inset in Fig. 7a] nearly linearly increases with the reaction time. The undetectable H$_2$ at the initial stage the VB offset for the Ga$_2$S$_3$/GaAs (111) heterostructure, which is 0.6 eV with the VBM of Ga$_2$S$_3$ lower than that of GaAs. In consequence, the conduction-band offset, in terms of Eq. 2, is 1.18 eV, assuming that the bandgap energies of GaAs and Ga$_2$S$_3$ are 1.42 and 3.20 eV, respectively. It is thus obvious that a type-I heterojunction is formed in the epitaxial Ga$_2$S$_3$/GaAs (111) heterostructure.
of reaction could be attributed to the system stabilization (e.g., gas dilution in the chamber) and/or the limitation of the detector. Figure 7b shows the photocurrent profile under chopped-illumination and biased at 0 V versus Ag/AgCl, which provides evidence for the stable photocurrent at the initial stage of gas evolution reactions. It has to be noted that the oxygen evolution is too weak for quantitative analysis. Morphology evolutions (SEM images not shown) after the two-hour testing revealed that the reaction on the Ga2S3/GaAs photoanode is dominated by photocorrosions of Ga2S3. The large amount of Ga vacancies in Ga2S3, having the defect levels located at 0.4–0.7 eV above its VBM,6,7 can compensate the VB offset and lead to the hole transfers freely from GaAs to Ga2S3. Electrocatalyst, for example, those of patterned Ni islands introduced by Hu et al.3 onto the surface of amorphous TiO2 coated on Si or the ultrathin Ni overlayers on GaAs, can be used to enhance the oxygen evolution on the surface of Ga2S3/GaAs photoanode, which, however, is still in progress.

In conclusion, cubic Ga2S3 layers have been epitaxially grown on n-GaAs (111) substrates by sulfurization. The epitaxial relationship, [110]Ga2S3(111)//[\text{110}]GaAs(111), has been determined by HRXRD, which is consistent with the collective in-plane orientation of the surface triangle structures of Ga2S3. The submicron triangle structures, clustered by nanoparticles of smaller than 50 nm in diameters, significantly reduced the reflectance of GaAs. Although the lattice mismatch between cubic Ga2S3 and GaAs is quite large, the Ga2S3 layer, nearly completely relaxed in the crystal lattices, is crack-free and exhibits a mirror-like surface. A valence-band offset of 0.6 eV has been measured by XPS for the Ga2S3/GaAs (111) heterostructure. Such a Ga2S3 layer, coated on n-GaAs (111) substrates, significantly enhanced the photocurrent when working as a photoanode. This effect has been attributed to the largely reduced surface reflectance as well as to the increased surface reaction/corrosion area. Although the hydrogen evolution on the counter electrode is apparent and stable after the system stabilization for about 1 hour, the oxygen evolution on the working electrode is very weak due to the lack of electrocatalyst.

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This is a symmetric configuration with the incident and diffracted x-ray beams having the same angle from the surface plane while the surface normal is tilted away from the beam plane formed by the incident and diffracted beams.

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