Energetic Sulfide Vapor-Processed Colloidal InAs Quantum Dot Solids for Efficient Charge Transport and Photoconduction

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The energetic sulfide vapor process on colloidal indium arsenide (InAs) quantum dots (QDs) for integrated optoelectronic devices is demonstrated. X-ray photoemission spectroscopy supports the presence of sulfur on QD surface, which increases the air stability, and ultraviolet photoemission spectroscopy and field-effect transistor analysis confirm n-type charge transport of corresponding QD films with higher electron mobilities. Photoconductivity of the same devices in near-infrared wavelength shows gate bias-dependent recombination of photo-generated carriers, coming from charge accumulation and depletion transition of QD channels. The synergetic approach of the vapor process on colloidal QD solids opens a promising opportunity for scalable and complementary metal-oxide semiconductor-compatible optoelectronic devices.

1. Introduction

The integration of III–V semiconductors on silicon discloses promising possibilities for next-generation optoelectronic devices due to their direct bandgap and efficient light emission and detection. Vapor deposition methods such as chemical vapor deposition or molecular beam epitaxy become well-established production technologies, but there are remaining challenges such as lattice mismatch and high fabrication cost under vigorous processing conditions, increasing safety and environmental concerns.

Colloidal synthesis of semiconductors can be an alternative approach for their easy fabrication and good control over their size and morphology without any concern on lattice mismatch with substrates or extreme reaction environment compared with vapor deposition method. Especially colloidal indium phosphide (InP) quantum dots (QDs) have gained a lot of attention in the display industry and market, as well as increasing number of research has been done for colloidal QD-based optoelectronic applications from light-emitting diodes and photovoltaics to lasers and photodetectors.

One challenge of colloidal semiconductors is their surface ligand, which is critical to control their crystal growth but causes poor charge transport in their solid state. Enhancing charge transport of QD solids is key to realize solid-state optoelectronic devices, and surface processing has been developed in a manner of the ligand exchange process using short-chain ligands such as thiol or halide ions. While these have successfully improved their charge transport, the covalent nature of III–V semiconductors requires higher energies of defect elimination and surface passivation. Epitaxial growth of III–V crystals requires higher processing temperatures—typically at least 500°C—compared with 250–450°C for II–VI crystals.

Surface trap energy of 3 nm InP QD is much higher than that of the same size of CdSe QDs, suggesting deeper trap states of InP QD. Furthermore, elements in group III and V have high oxophilicity, causing significant oxidation upon exposure to oxygen environments. A few surface treatments have been studied for III–V QDs such as HF and NOBF4 processing to remove surface hydroxide and oxide of InP and InAs QDs, respectively, which could require further surface reconstruction to improve passivation and charge transport especially for InAs QD.

As there is a limitation on using solution-phase processing due to lower boiling temperature and reactivity of common solvents and chemicals, gas-phase processing for QD solids would be a good candidate. Atomic layer deposition has been done for QD solids in which deposition of the inorganic matrix on QD surfaces increases their carrier mobility with better surface passivation and absorption coefficient but causes reduced photosponse or negative photocurrent. This remains challenging for QD-based optoelectronic applications, and so far other types of surface processes in gas phase have never been done with III–V QD materials. To realize enhanced charge transport with preserved optoelectronic properties of III–V QDs, we introduce sulfide vapor processing under the condition of chemical vapor deposition after NOBF4 treatment of InAs QDs as shown in Figure 1. They are exposed to H2S gas at high temperature (150–250°C), which sulfidates the surface of InAs QDs,
supported by X-ray photoemission spectroscopy (XPS), and provides additional stability in ambient conditions. Ultraviolet photoemission spectroscopy (UPS) and field-effect transistor (FET) measurement shows robust n-type charge transport with enhanced electron mobilities. Furthermore, photocurrent measurement in the near-infrared region confirms our development on QD surface processing and enhances their photocarrier extraction, in which gate voltage of FET changes charge depletion to the accumulation mode of QD channel and monomolecular carrier recombination to bimolecular recombination as well.

2. Results and Discussion

2.1. Surface Chemistry of Sulfide Vapor-Processed Colloidal InAs QD Solids

It is known that as-synthesized QDs have long alkyl chain ligands on their surface, and NOBF₄ treatment removes them as well as surface oxide and transfers QDs into polar solvents such as dimethylformamide (DMF). This is beneficial in enhancing interparticle coupling in QD films for charge transport in solid-state devices, but it is still vulnerable in ambient conditions to oxidize their surface. InAs QD under this condition is termed “InAs⁰.” To prepare sulfide vapor-processed colloidal InAs QD solids, InAs⁰ in DMF solution is coated on a substrate to make a ≈36 nm-thick film. QD samples are transferred to the quartz tube in the furnace under N₂ atmosphere and heated to 150–250 °C with a supply of H₂S gas for 10 min. They are cooled to room temperature and show no serious damage or change in their morphology, as shown in Figure 2a.

Previously, when coupled QD solids were fabricated at high temperatures, their charge transport was much enhanced but sometimes they lost quantum confinement and became bulk state.¹⁶,¹⁷ Our ensemble absorption spectra show resolved excitonic transitions in Figure 2b, and the 1s absorption peak is shifted from 1080 nm of InAs⁰ to 1077 nm of sulfide vapor-processed QD at 150 °C (this is termed “S-InAs¹⁵₀”) and 1055 nm at 250 °C (this is termed “S-InAs²⁵₀”). According to the sizing curve of InAs QDs, InAs⁰ is 5.28 nm in diameter, and S-InAs¹⁵₀ and S-InAs²⁵₀ are 5.26 and 5.11 nm, respectively. As the lattice constant of InAs is 0.606 nm for zinc blende structure, InAs⁰ and S-InAs²⁵₀ have the same size within 3.3% difference in the size of one unit cell. For S-InAs²⁵₀, the size difference is 0.17 nm, corresponding to 28.1% of one unit cell, so it is possible to assume that one atomic layer is replaced or missed by the sulfide vapor process. Figure 2c shows X-ray diffraction (XRD) patterns of naked and H₂S-treated InAs QD films, confirming that the crystal structure does not change upon sulfide vapor process.

XPS is a powerful technique to explore the surface chemistry of colloidal QDs. Figure 2d shows As 3d spectra with a strong arsenic oxide peak in 45 eV from naked InAs QDs when exposed to air, which is consistent with other reports showing oxidized As 3d core levels at the same position for surface oxidation of InAs QDs. Sulfur passivation has been explored in various literatures.²⁰,²¹ Surface oxide can be removed by introducing sulfur onto III–V semiconductors, sulfide passivation has been explored in various literatures.²⁰,²¹ Surface oxide can be removed by introducing sulfur onto III–V semiconductors, accompanied with high-temperature annealing or UV radiation and followed by sulfide ions passivating their surface dangling bonds. In our case, H₂S gas can bring sulfide ions on the surface of InAs QDs and replace oxide to sulfide when the samples are already exposed to air to create arsenic oxide. Once sulfide ions passivate the surface of InAs, it can prevent further oxidation by surface In–S moieties, which are beneficial in keeping their intrinsic electronic properties and fabricating solid-state devices with good stability. The presence of sulfide is confirmed by XPS data (Figure S1, Supporting Information), with the peak shift of In 3d and As 3d as well.

Figure 1. Schematic of sulfide vapor processing for InAs QD film in furnace under carrier gas (5% of H₂S in N₂). Inset shows that hydrogen sulfide gas vapor generates sulfur-terminated InAs QD surface.
as increased intensities of S 2p. The decreased intensity of As 3d implies there is a possible replacement between As and S from InAs QDs. The previous study of Sandroff et al. showed two types of As—S bonds, one is a disulfi de bond of As—(S—S) with S/C01 and the other is As2S3 of S/C02.[22] The former has the energy shift from the bulk As of 1.5–1.6 eV, and the latter has that of 2.4–2.7 eV, respectively. As sulfi de vapor-processed InAs QD has the energy shift of 1.5 eV, As atoms could be bound with disulfi de or polymeric S atoms. This might be the reason of excess amount of sulfur observed in our InAs QD solids, embedded in the sulfi ur-based network of inorganic matrix.

2.2. Charge Transport of H2S-Treated InAs QD Solids in the Dark and under Light Illumination

UPS allows to explore the electronic states of materials such as Fermi levels and valence band (VB) maxima, and the conduction band (CB) minima can be estimated by adding the optical bandgap determined from absorption spectra.[39] Compared with InAs0, S-InAs150 and S-InAs250 show Fermi levels that are close to their CB minima (Figure S2, Supporting Information), suggesting n-type behavior of corresponding QD solids. To understand electronic properties of sulfi de vapor-processed InAs QDs, FET devices based on QD films are used. Briefly, source and drain electrodes are deposited on thermally grown SiO2 as a dielectric layer on a heavily doped Si wafer as a gate electrode. InAs0 solution is spin coated on the wafer, and sulfi de vapor process is done with 150 and 250 °C processing temperatures, as described earlier. The device is analyzed using a semiconductor analyzer at room temperature. Figure 3a shows the representative drain current–gate voltage (Ids–Vg) characteristics of sulfi de vapor-processed InAs QD FETs. The increase in Ids with positive Vg indicates typical n-type transport characteristic of QD fi lms, in which the positive gate bias induces the accumulation mode of electron majority carriers and increases the drain current. The electron mobilities of InAs QD FETs (μ) are determined using the gradual channel approximation equation in the linear regime.

\[
\mu = \frac{(dI_{ds}/dV_g) L}{m W CV_{ds}}
\]  

where L and W are the channel length and width, m is the number of the channels, C is the capacitance per unit area of the gate oxide (13.8 nF cm⁻²), and Vds is the drain voltage. The calculated electron mobilities are \(4.8 \times 10^{-5}\) and \(1.7 \times 10^{-3}\) cm²Vs⁻¹ for S-InAs150 and S-InAs250, respectively. In contrast, the FET of InAs0 shows very low current even with high gate bias probably because NOBF4 treatment does not passivate deep trap states but only removes organic ligands, so its defective surface suppresses effi cient charge transport. As InAs0 film requires heating process at 150 °C to remove residual DMF solvent, this dramatic change of

Figure 2. a) Transmission electron microscopy image of sulfi de vapor-processed InAs QD fi lm. b) Absorption spectra of InAs0, S-InAs150 and S-InAs250 fi lms. The vertical dashed line is a guide for the eye to clarify the shift of absorption peaks. c) XRD patterns of InAs0, S-InAs150 and S-InAs250 fi lms. The vertical lines show the corresponding positions and intensities for bulk InAs. A sharp peak from the naked InAs QD originates from the substrate, which does not depend on the sample properties. d) XPS data showing the As 3d spectra of InAs0 fi lm with strong As2O3 peak when exposed to air (for 2 h). In contrast, S-InAs150 and S-InAs250 fi lms show much less oxidation and good air stability.
their electric properties is not just from heating but more from the sulfide process.

Figure 3b shows a model for the electronic structures of InAs0 film and sulfide vapor-processed InAs QD film. InAs0 film has a deep in-gap state which suppresses the charge transport; even NOBF₄ treatment removes organic ligands from QD surface. Sulfide vapor process introduces shallow states near the CB, so they have less transport barrier energy than the deep in-gap state of InAs₀ film, improving electron transport in FET devices with higher mobilities. There are examples of introducing shallow states in the energy level for high mobilities in QD solids, with various surface processes controlling their doping, Fermi level, and transport properties.[23,24]

Photoresponses to external illumination of InAs QD devices are tested using the same FET devices. InAs QD layers absorb the incident light and generate photocarriers, which are transported to the source and drain electrodes under the control of the gate voltages. The photocurrent \( I_{\text{photo}} = I_{\text{light}} - I_{\text{dark}} \), in which \( I_{\text{light}} \) is current under light illumination and \( I_{\text{dark}} \) is the current in the dark. One of the important figures of merit for photodetection application is the signal-to-noise ratio (SNR), which can be defined as \( I_{\text{photo}}/I_{\text{dark}} \). Figure 3c shows the effect of a gate voltage applied between the metal and the QD layers, and although dark current and photocurrent are higher for positive gate voltage, higher SNR comes from negative gate voltage or the depletion regime of FET operation. This can be understood of the impact of dark current or noise level for the devices, which can give the maximum sensitivity of photodetection.[25,26]

To explore the detailed mechanism of photoconduction for the corresponding FET, power-dependent photocurrent responses are measured depending on gate bias. Figure 3d shows the photocurrent of InAs QDs as a function of the illumination intensity, in which the photocurrent increases with higher light intensity. The nonlinearity of light intensity \( P \)–photocurrent is analyzed by applying a power law, as shown in the following equation.

\[
I_{\text{photo}} \propto P^{\alpha}
\]

where \( \alpha \) is the dimensionless exponent of the power law, which is expected to be 1, if first-order monomolecular (i.e., geminate or trap-assisted) recombination process is dominating.[27] When the value is close to 0.5, bimolecular recombination mechanism is dominant. Our measured exponent \( \alpha \) is 0.64 with \( V_g = 25 \text{ V} \) and 1.03 and with \( V_g = -25 \text{ V} \), implying that charge recombination mechanism depends on the gate bias in which the accumulation mode prefers bimolecular recombination and depletion mode prefers monomolecular recombination.

Figure 4 shows the charge transfer mechanism of InAs QDs in the dark and under illumination conditions, to explain different behaviors of gate bias dependences using the band diagram of metal–oxide–semiconductor structures. In the case of an n-type InAs QD in the dark, a positive gate voltage induces electron accumulation in the channel with high drain current (Figure 4a).
With light illumination, photogenerated carriers will increase the total number of carriers but the channel is already filled, and the current increase is not significant (Figure 4b).

If a negative gate bias is applied, band bending changes direction and leads to depletion of electrons near the oxide layer, decreasing the drain current as well (Figure 4c). This will decrease dark current or noise level of photodetection mode, which is important in the photosensitivity of the device. Once light illumination can generate excitons in the channel under this condition, photogenerated electrons contribute to the total number of carriers and increase the drain current dramatically (Figure 4d).

3. Conclusion

We demonstrated sulfide vapor-processed colloidal InAs QDs and investigated their characteristic properties as well as fabricated thin-film devices using FET geometry with enhanced charge transport and photoresponse. Increased S on the surface of QDs was confirmed by XPS, which also improved the air stability under ambient conditions. n-type charge transport was confirmed with sulfide vapor-processed InAs QDs, and further photocurrent measurement using near-infrared illumination shows photoconduction behavior of the corresponding FET device with gate bias-dependent charge recombination process. Our unique approach combining the solution process of colloidal semiconductor nanocrystals and surface process in the vapor phase opens a promising opportunity for scalable integrated optoelectronic applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

colloidal quantum dots, field-effect transistors, indium arsenide, photoconduction, vapor processes

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[1] Y. Hu, D. Liang, K. Mukherjee, Y. Li, C. Zhang, G. Kurczweil, X. Huang, R. G. Beausoleil, Light Sci. Appl. 2019, 8, 93.
[2] S. Mauthe, Y. Baumgartner, M. Sousa, Q. Ding, M. D. Rossell, A. Schenk, L. Czornomaz, K. E. Moselund, Nat. Commun. 2020, 11, 4565.
[3] S. Chowdhury, A. Das, P. Banerji, AIP Conf. Proc. 2018, 1953, 30233.
[4] C. R. Kagan, E. Lifshitz, E. H. Sargent, D. V Talapin, Science 2016, 353, aac5523.
[5] Y.-H. Won, O. Cho, T. Kim, D.-Y. Chung, T. Kim, H. Chung, H. Jang, J. Lee, D. Kim, E. Jang, Nature 2019, 575, 634.
[6] T. Kim, S. Lim, S. Yun, S. Jeong, T. Park, J. Choi, Small 2020, 16, 2002460.
[7] Y.-S. Park, J. Roh, B. T. Diroll, R. D. Schaller, V. I. Klimov, Nat. Rev. Mater. 2021, 6, 382.
[8] F. P. García de Arquer, A. Armin, P. Meredith, E. H. Sargent, Nat. Rev. Mater. 2017, 2, 16100.
[9] J. H. Song, H. Choi, H. T. Pham, S. Jeong, Nat. Commun. 2018, 9, 4267.
[10] L. Asor, J. Liu, Y. Ossia, D. C. Tripathi, N. Tessler, A. I. Frenkel, U. Banin, *Adv. Funct. Mater.* 2021, 31, 2007456.

[11] V. Srivastava, W. Liu, E. M. Janke, V. Kamysbayev, A. S. Filatov, C.-J. Sun, B. Lee, T. Rajh, R. D. Schaller, D. V Talapin, *Nano Lett.* 2017, 17, 2094.

[12] Y. Kim, J. H. Chang, H. Choi, Y.-H. Kim, W. K. Bae, S. Jeong, *Chem. Sci.* 2020, 11, 913.

[13] T.-G. Kim, D. Zherebetskyy, Y. Bekenstein, M. H. Oh, L.-W. Wang, E. Jang, A. P. Alivisatos, *ACS Nano* 2018, 12, 11529.

[14] A. Pourret, P. Guyot-Sionnest, J. W. Elam, *Adv. Mater.* 2009, 21, 232.

[15] Y. Liu, M. Gibbs, C. L. Perkins, J. Tolentino, M. H. Zarghami, J. Bustamante, M. Law, *Nano Lett.* 2011, 11, 5349.

[16] A. W. Wills, M. S. Kang, A. Khare, W. L. Gladfelter, D. J. Norris, *ACS Nano* 2010, 4, 4523.

[17] D. S. Dolzhnikov, H. Zhang, J. Jang, J. S. Son, M. G. Panthani, T. Shibata, S. Chattopadhyay, D. V Talapin, *Science* 2015, 347, 425.

[18] T. Kim, S. Park, S. Jeong, *Nat. Commun.* 2021, 12, 3013.

[19] J. Leemans, K. C. Dümbgen, M. M. Minjauw, Q. Zhao, A. Vantomme, I. Infante, C. Detavernier, Z. Hens, *J. Am. Chem. Soc.* 2021, 143, 4290.

[20] K. Banerjee, S. Ghosh, E. Plis, S. Krishna, *J. Electron. Mater.* 2010, 39, 2210.

[21] S. Tian, Z. Wei, Y. Li, H. Zhao, X. Fang, J. Tang, D. Fang, L. Sun, G. Liu, B. Yao, X. Ma, *Mater. Sci. Semicond. Process.* 2014, 17, 33.

[22] C. J. Sandroff, M. S. Hegde, L. A. Farrow, C. C. Chang, J. P. Harbison, *Appl. Phys. Lett.* 1989, 54, 362.

[23] C. R. Kagan, C. B. Murray, Nat. Nanotechnol. 2015, 10, 1013.

[24] H. Wang, D. J. Butler, D. B. Straus, N. Oh, F. Wu, J. Guo, K. Xue, J. D. Lee, C. B. Murray, C. R. Kagan, *ACS Nano* 2019, 13, 2324.

[25] D. Kufer, T. Lasanta, M. Bernechea, F. H. L. Koppens, G. Konstantatos, *ACS Photonics* 2016, 3, 1324.

[26] X. Yin, C. Zhang, Y. Guo, Y. Yang, Y. Xing, W. Que, *J. Mater. Chem. C* 2021, 9, 417.

[27] L. J. Willis, J. A. Fairfield, T. Dadosh, M. D. Fischbein, M. Drndic, *Nano Lett.* 2009, 9, 4191.