

Silver Ions as Ambipolar Dopants in InAs Nanocrystal Solids

Hwichan Cho, Hyoin Kim, Meeree Kim, Mahnmin Choi, Hyunwoo Jo, Da In Kim, Byeongjae Kang, SeungHwan Roh, Hyunjung Kim, Ji-Sang Park,* Sohee Jeong,* and Moon Sung Kang*

The precise control of semiconductor polarity in nanocrystals (NCs) is crucial for optimizing device performance in various optoelectronic applications. In this study, it is shown that Ag^+ , added post-synthetically to InAs NCs using an AgNO_3 solution, can induce either *n*-type or *p*-type doping of the solid, depending on the intrinsic polarity of the host and the dopant concentration. In *n*-type InAs NCs, Ag^+ consistently acts as an interstitial *n*-type dopant, shifting the conduction band minimum closer to the Fermi level. Conversely, in *p*-type InAs NCs (innately doped with Zn during synthesis), Ag^+ initially exhibits a *p*-type doping effect at low concentrations by forming surface dipoles but transitions to an *n*-type doping effect at higher concentrations through interstitial incorporation. These results offer a unified understanding of the intricate and adjustable doping behavior of Ag^+ in colloidal NC systems and present new opportunities for post-synthetic polarity engineering in III–V nanomaterials.

based on NCs, controlling the semiconductor polarity of NCs is crucial.^[3,4] The semiconductor polarity not only determines the optimal device structure but also influences the selection of other functional materials used in the devices.^[5–8] Similar to bulk semiconductors, the polarity control of NCs is achieved through doping, which involves intentionally introducing impurities to the host semiconductors to alter their electrical properties.^[9,10] Unlike the conventional silicon doping with neutral atoms (e.g., neutral boron atom for *p*-type doping and neutral phosphorus atom for *n*-type doping in silicon), doping in NCs typically involves cations rather than neutral atoms, which are introduced either during the synthesis of NCs or through post-synthetic steps.^[9,11–13] For example, consider the incorporation of a monovalent

cation into a III–V NC. Unlike a monovalent neutral atom, the monovalent cation lacks an extra valence electron. If a monovalent cation occupies an interstitial site in the III–V host semiconductor lattice, it would not directly affect the Fermi level (E_F) of the host, because it cannot contribute valence electrons.^[14–17] However, the positive potential of the cation lowers the positions of the conduction band minimum (CBM) and the valence band maximum (VBM).^[16] This leads to an increase in the electron concentration within the NC (which is determined by the offset

1. Introduction

Semiconductor nanocrystals (NCs) are promising materials for electronic and optoelectronic devices due to their size-dependent electronic and optical properties, as well as their compatibility with large-scale solution processing techniques.^[1] These properties make NCs suitable for a wide range of optoelectronic devices such as light-emitting diodes, photodetectors, photovoltaics, and thin-film transistors.^[2] To achieve high-performance devices

H. Cho, H. Jo, D. I. Kim, S. Roh, M. S. Kang
Department of Chemical and Biomolecular Engineering
Sogang University
Seoul 04107, Republic of Korea
E-mail: kangms@sogang.ac.kr
M. S. Kang
Institute of Emergent Materials
Sogang University
Seoul 04107, Republic of Korea

H. Kim, M. Kim, M. Choi, S. Jeong
Department of Energy Science (DOES) and Center for Artificial Atoms
Sungkyun Institute of Energy Science and Technology (SIEST)
Sungkyunkwan University
Suwon 16419, Republic of Korea
E-mail: s.jeong@skku.edu

S. Jeong
Department of Future Energy Engineering (DFEE)
Sungkyunkwan University
Suwon 16419, Republic of Korea

B. Kang, H. Kim
Center for Ultrafast Phase Transformation
Department of Physics
Sogang University
Seoul 04107, Republic of Korea

J.-S. Park
SKKU Advanced Institute of Nanotechnology (SAINT) and Department of
Nano Engineering
Sungkyunkwan University
Suwon 16419, Republic of Korea
E-mail: jisangpark@skku.edu

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adma.202514750>

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between E_F and CBM), creating an n -doping effect.^[18] In contrast, if the monovalent cation substitutes for a Group III cation in the III-V host semiconductor lattice (i.e., occupies a substitutional site), it forms an effectively negative potential, which raises the positions of CBM and VBM.^[9,16,17] As the relative offset between E_F and VBM decreases, the hole concentration within the NC increases, resulting in a p -doping effect. Moreover, if a cation binds to the surface of NCs instead of integrating into the lattice, it can influence the electronic structure of NCs by passivating defects on the surface or by inducing surface dipoles.^[19–24] Overall, the method of monovalent cation doping in NCs can lead to varied effects on the electronic properties of NCs, including their semiconductor polarity.

In this study, we present that Ag^+ ions that are post-synthetically introduced to InAs NC films can serve as ambipolar dopants (meaning that they function as either p - or n -type dopants) to the host, depending on the original semiconductor polarity of the host NCs as well as on the amount of dopants introduced. This differs from a previous report that presented silver (not specified as a cation or a neutral atom) simply serving as a p -type dopant to InAs NCs through substitutional doping on the In site.^[25] We observed that Ag^+ applied to originally n -type InAs NC thin films yields an n -type doping effect. Conversely, when the same Ag^+ was applied to originally p -type InAs NC thin films (which are inherently doped with Zn from the synthesis), it acted as a p -type dopant at low concentration but transitioned to an n -type dopant at higher concentration. The incorporation of Ag^+ into different InAs NCs was systematically investigated. We believe that this understanding enables the fine-tuning of InAs NC characteristics for various high-performance near-infrared (NIR) optoelectronic devices.^[26,27]

2. Results

Silver doping was applied to two different InAs NCs with opposite semiconductor polarities inherently determined during synthesis (Figure 1a). The p -type InAs NCs, capped with oleylamine (OLA), were synthesized using indium chloride ($InCl_3$) and tris(dimethylamino)arsine (DMA-As) precursors.^[9] In this case, the p -type characteristic was achieved by utilizing diethylzinc (Et_2Zn) as the reducing agent to activate DMA-As precursor, which also introduces Zn into the InAs lattice, serving as an acceptor. Previous research^[9] indicated that Zn introduced during the synthesis could be incorporated either within the lattice or on the surface of InAs. It was found that the Zn fraction substituting the In sites within the lattice acted as acceptors for the host NC. On the other hand, the n -type InAs NCs, capped with OLA ligands, were synthesized using indium (I) chloride ($InCl$) and DMA-As precursors (without Et_2Zn).^[28] Scanning transmission electron microscopy (STEM) images of the resulting NCs are shown in Figure S1 (Supporting Information). Thin films of these InAs NCs, treated with 1,2-ethanedithiol (EDT),^[24,29] exhibited comparable electron and hole field-effect mobilities ($\mu_e = (5.7 \pm 0.4) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\mu_h = (1.7 \pm 0.1) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), which are also comparable to values reported from previous EDT-treated InAs NCs (Table S1, Supporting Information). The experimental section provides detailed information on the synthetic process and fabrication steps of the field-effect transistors (FETs).

Silver doping was performed on solid-phase thin films of both p - and n -type NCs (that had been pretreated with EDT) using $AgNO_3$ solutions in acetonitrile at varying concentrations (Figure 1a). In the solution, $AgNO_3$ exists as Ag^+ and NO_3^- , with the cation Ag^+ being introduced into InAs NCs for doping, not the neutral Ag atom. Figure 1b shows a series of UV-Vis-NIR absorbance spectra for the n -type InAs NC films doped at different $AgNO_3$ concentrations (in the range of 10^{-2} – $10^{-1.5} \text{ mg mL}^{-1}$). Results obtained using even higher $AgNO_3$ concentrations are discussed in a later section. The bandgap was determined from the minimum point in the 2nd derivative of the curve, since the characteristic first excitonic transition peak was not evident in the spectrum. A gradual decrease in the bandgap (from 1.09 to 1.03 eV) was observed with higher concentrations of $AgNO_3$ solutions, indicating the formation of dopant states within the bandgap. The positions of the CBM, E_F , and VBM of the n -type InAs NC film after doping with $AgNO_3$ solutions ($10^{-1.5} \text{ mg mL}^{-1}$) are compared with those of the pristine NC film in Figure 1c. X-ray photoelectron spectroscopy (XPS) analysis revealed that the atomic composition of Ag relative to As in this doped NC film is 14%. Although XPS is a surface-sensitive technique that probes primarily the top few nanometers of the film, we conjecture that the composition attained from XPS reflects the composition of the entire NC film, since Ag^+ ions introduced via $AgNO_3$ infiltration can diffuse uniformly throughout the porous NC film. The E_F was determined from Kelvin probe measurement, the position of VBM was determined from ambient-pressure photoelectron yield spectroscopy (PYS), and the position of CBM relative to VBM was determined from the bandgap obtained from UV-Vis-NIR absorbance analysis. The CBM position was found to move closer to E_F upon Ag^+ doping, reducing the offset between CBM and E_F from 0.30 eV in the pristine n -type InAs NC film to 0.21 eV in the Ag^+ -doped InAs NC film ($Ag/As = 14\%$), indicating an n -type doping effect.

The resulting impact of Ag^+ doping on the n -type InAs NC films could be directly confirmed through electrical transport measurements using a FET device testbed. Figure 1d displays a set of transfer characteristics (drain current (I_D) versus gate voltage (V_G)) relations at a fixed drain voltage ($V_D = \pm 60 \text{ V}$) in the saturation regime) of the FETs based on n -type InAs NC films. The transfer characteristics of these devices collected in the linear regime ($V_D = \pm 2 \text{ V}$) are plotted in Figure S2 (Supporting Information). Treatment with $AgNO_3$ resulted in a negative shift in the transfer characteristics, along with a decrease in the threshold voltage (V_T) and an increase in the current level, indicative of an n -doping effect on the channel. Note that the channel current (i.e., I_D) was substantially larger than the gate current (Figure S3, Supporting Information), indicating that the measurement I_D originates from the channel conduction rather than leakage. The evolution in the transfer characteristics was observed to be gradual with an increase in the concentration of the applied $AgNO_3$ solution. The electron mobility (μ_e) values extracted from the current-voltage (I - V) characteristics showed a gradual variation with the increasing concentration of the $AgNO_3$ solution used for doping the films (Figure 1e). For Ag^+ -doped n -type InAs NC films (Ag/As ratio = 14%), saturation μ_e increased by a factor of five to $(3.7 \pm 0.2) \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (compared to $(5.7 \pm 0.4) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ before doping). These results suggest that the introduction of Ag^+ to the thin films of n -type InAs NCs induces an

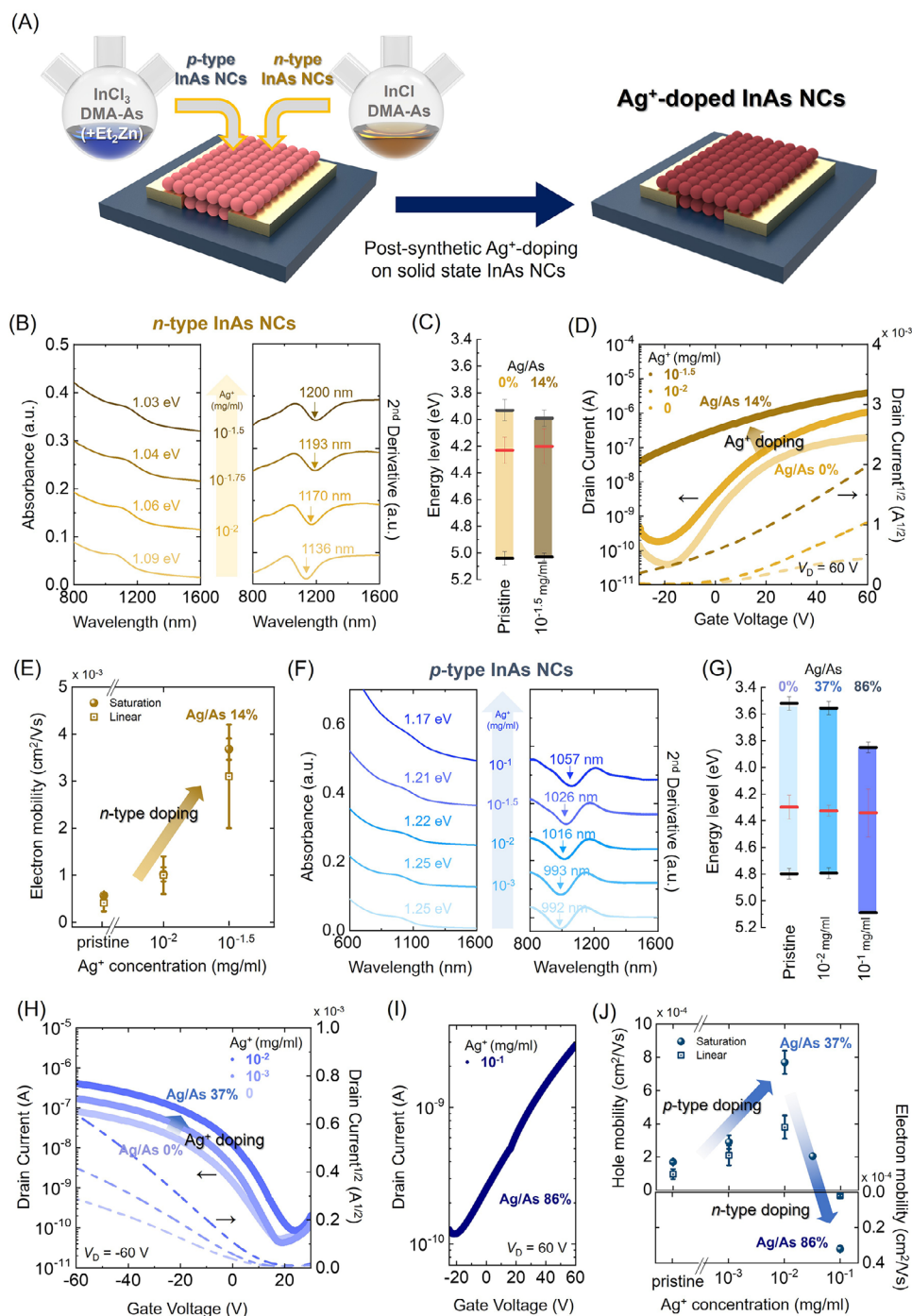


Figure 1. a) Schematic of the Ag⁺ doping process for p-type and n-type InAs NC solids. b) Absorbance spectra of n-type InAs NC films doped with varying concentrations of Ag⁺. c) Energy level diagrams of n-type InAs NC films doped with varying concentrations of Ag⁺. d) Transfer characteristics of FETs based on (originally) n-type InAs NC films before and after doping with Ag⁺ at different concentrations. e) Summary of electron mobilities of Ag⁺-doped n-type InAs NC films. f) Absorbance spectra of p-type InAs NC films doped with different concentrations of Ag⁺. g) Energy level diagrams of p-type InAs NC films doped with varying concentrations of Ag⁺. h) Transfer characteristics of FETs based on (originally) p-type InAs NC films before and after Ag⁺ doping at low concentrations (up to Ag/As = 37%). i) Transfer characteristics of FETs based on (originally) p-type InAs NC films heavily doped with Ag⁺ (Ag/As = 86%). j) Summary of carrier mobilities of Ag⁺-doped p-type InAs NC films (saturation and linear mobility values were collected at V_D = ±60 V and ±2 V, respectively).

n-doping effect. It is important to note that this observation differs from a previous study on InAs NCs in dispersion treated with AgNO₃, which exhibited a significant *p*-type doping effect as confirmed by density of states measurements using scanning tunneling spectroscopy.^[25] When the films were treated with higher concentrations of AgNO₃, as reported in previous studies, the FET current decreased substantially (Figure S4, Supporting Information). The extracted saturation μ_e decreased to $(1.3 \pm 0.2) \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, indicating that excessive introduction of Ag⁺ may suppress electron transport characteristics. Under such high doping conditions, Ag⁺ could potentially degrade the *n*-type InAs NCs or act as a *p*-type dopant, as reported by Banin et al.^[16,17,25]

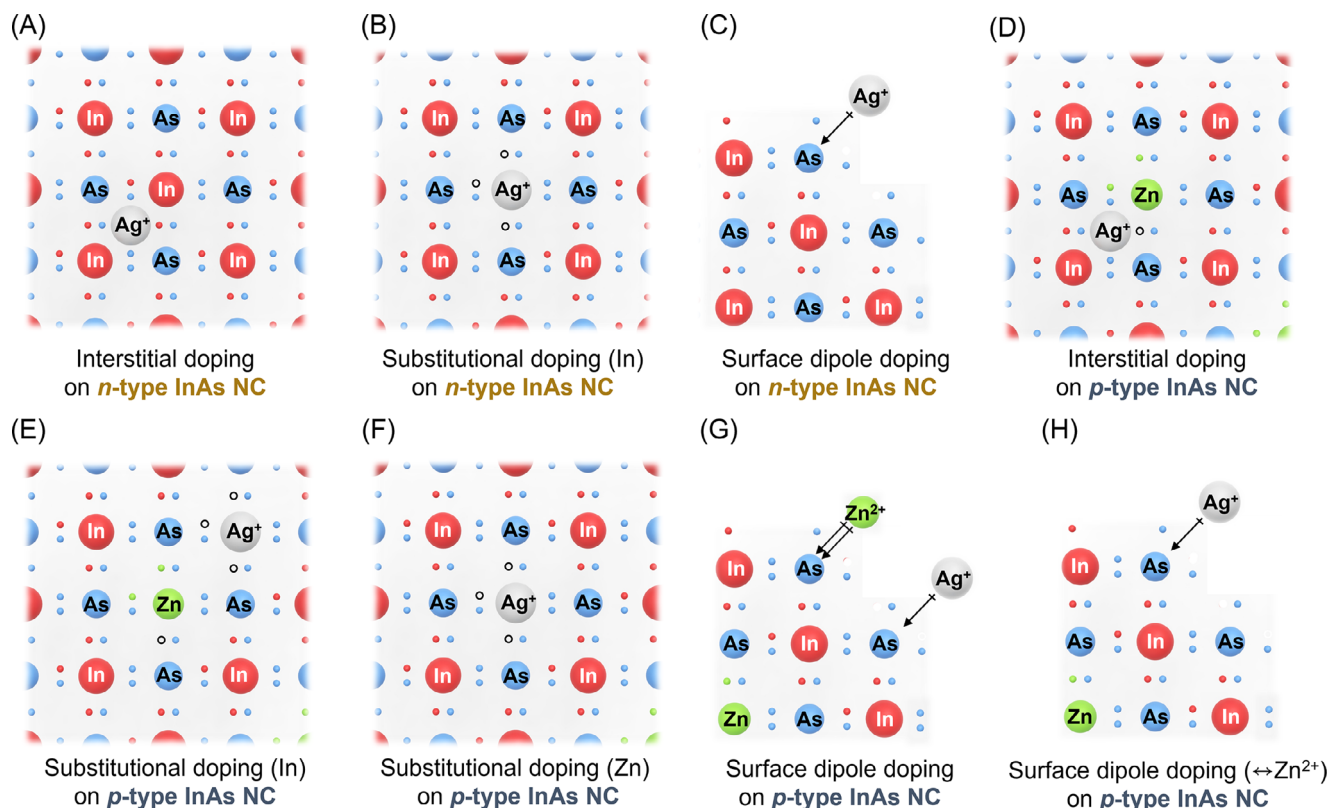
More noticeable changes in the electronic structures of NCs were observed in the *p*-type InAs NCs. Figure 1f displays a series of UV-Vis-NIR absorbance spectra for the *p*-type InAs NC films doped at varying concentrations. At low doping concentrations (up to $10^{-2} \text{ mg mL}^{-1}$, resulting in an Ag/As ratio of 37%), a slight reduction in the bandgap (from 1.25 to 1.22 eV) was achieved. With higher doping concentrations (resulting in an Ag/As ratio of 86%), the bandgap further decreased to 1.17 eV. This gradual bandgap trend was consistent with the results from the *n*-type InAs NC films. However, a distinct change was observed in the absolute position of the energy levels, particularly under high doping conditions (Figure 1g). While E_F remained relatively constant across the doping range, the positions of the CBM and VBM shifted significantly downward, especially under high doping conditions, contrasting with the marginal shift under low doping conditions. These results suggest that Ag⁺ plays distinct roles under these two doping conditions. Moreover, the shift in the CBM, E_F , and VBM collectively positioned the E_F closer to the VBM under low doping conditions (indicating *p*-type characteristics), whereas under high doping conditions, the E_F was closer to the CBM (suggesting *n*-type characteristics for the NC films).

The intricate impact of Ag⁺ doping on *p*-type InAs NCs was directly assessed through electrical characteristics measurements using an FET testbed. Figures 1h, S5 (Supporting Information), and Figure 1i display a series of transfer characteristics of the FETs based on *p*-type InAs NCs doped with varying concentrations of AgNO₃. It was observed that increasing the AgNO₃ concentration up to $10^{-2} \text{ mg mL}^{-1}$ (resulting in an Ag/As ratio of 37%) led to a gradual positive shift in the transfer characteristics of the FETs. This shift was accompanied by a positive change in V_T and an increase in current levels, both indicative of a typical *p*-doping effect on the channel. The values of hole mobility (μ_h) also increased gradually with higher Ag⁺ content in the films, up to a condition resulting in an Ag/As ratio of 37% (Figure 1j). Under these conditions, Ag⁺ acted as a *p*-type dopant in the *p*-type InAs NCs, which were already doped with Zn during synthesis. Upon treatment of the films with a higher concentration of AgNO₃ solution (e.g., $10^{-1.5} \text{ mg mL}^{-1}$), both the current level and the extracted saturation μ_h value decreased (Figures 1j; S5, Supporting Information), indicating that excessive introduction of Ag⁺ could deteriorate the *p*-type electrical characteristics. We conjecture that Ag⁺ at such concentrations primarily functions as an *n*-type dopant (further discussion is given below), potentially counteracting the *p*-type electrical characteristics of the given *p*-type NC films. When the films were exposed to even higher AgNO₃ concentrations (e.g., $10^{-1} \text{ mg mL}^{-1}$, resulting in an Ag/As ratio of 86%), the semiconductor characteristics of the InAs NC films,

initially exhibiting *p*-type behavior, transitioned to *n*-type characteristics (Figure 1i). These findings demonstrate that Ag⁺ can induce both *p*- and *n*-type doping effects on InAs NCs, depending on the introduced amount. This complete reversal in semiconductor polarity at the device level, particularly shifting from the original *p*-type characteristics to *n*-type characteristics through a post-synthetic heterovalent doping process, has not been previously achieved for thin films of NCs.

We emphasize that the intricate impact of Ag⁺ on InAs NCs differs from prior findings. Banin et al. previously documented Ag acting as a *p*-type dopant in InAs NCs, particularly when Ag⁺ is incorporated into the NCs via post-synthetic solution-state diffusion doping^[16,17,25] (the dopant in their study is denoted as Ag, but we interpret it as its ionic form since it originates from an AgNO₃ solution). While they did not assess the electrical transport properties of the doped InAs NCs, they noted a shift in the E_F closer to the VBM using scanning tunneling microscopy analysis, indicating the *p*-type doping induced by Ag⁺. Had they conducted electrical measurements, we predict that their Ag⁺ doping would have reduced the *n*-channel current of InAs NC films. They attributed the observed *p*-type doping to the substitutional doping of Ag replacing In.^[16] However, our results reveal that Ag⁺ can exhibit a more diverse and complex behavior toward InAs NCs. Indeed, the intricate doping effects of Ag⁺ (introduced to NCs via the AgNO₃ treatment) have been documented in originally *n*-type CdSe NCs by Norris et al.^[30] In their study, a low concentration of Ag⁺ induced *n*-type doping in CdSe NCs, while a high concentration led to *p*-type doping.

Therefore, we recommend a thorough investigation of the doping impact of Ag⁺ on our system, exploring various potential mechanisms through which Ag⁺ may interact with InAs NCs. These mechanisms include: Case 1, where Ag⁺ may occupy interstitial sites within the InAs NC lattice; Case 2, involving the substitution of In atoms in the lattice with Ag⁺; and Case 3, where Ag⁺ may be physically adsorbed on the surface of the InAs NCs. As previously discussed in the Introduction section, in Case 1, Ag⁺ would induce an *n*-doping effect on the InAs NCs by reducing both the VBM and CBM due to the positive potential introduced by Ag⁺ (Scheme 1a). Conversely, in Case 2, Ag⁺ would lead to a *p*-doping effect on the InAs NCs as the replacement of In with Ag⁺ (resulting in the release of In³⁺) generates a net negative potential, producing an effect opposite to that of Case 1 (Scheme 1b). In Case 3, Ag⁺ could induce a *p*-doping effect by creating a surface dipole pointing inward toward the NC core (Scheme 1c). A more diverse range of effects may be observed in InAs NCs already doped with Zn. These effects include: Case 1, where Ag⁺ occupies interstitial sites in the Zn-doped InAs NC lattice, resulting in an *n*-doping effect (Scheme 1d); Case 2, involving the substitution of In in the Zn-doped InAs NC lattice (releasing In³⁺), leading to a *p*-doping effect (Scheme 1e); Case 2', where Zn in the Zn-doped InAs NC lattice is substituted with Ag⁺ (releasing Zn²⁺), leading to a *p*-doping effect (Scheme 1f); Case 3, where Ag⁺ is physically adsorbed on the surface of the InAs NCs, inducing a *p*-doping effect (Scheme 1g); and Case 3', where Ag⁺ is adsorbed on the surface of the InAs NCs, replacing the existing Zn²⁺ and thereby counteracting the surface dipole *p*-doping effect exerted by the original Zn²⁺ (Scheme 1h). By systematically analyzing these various scenarios, we investigated the influence of Ag⁺ on two distinct InAs NC systems with opposite



Scheme 1. Illustration of the Ag^+ doping in *n*- and *p*-type InAs NCs, highlighting interstitial, substitutional, and surface doping mechanisms.

semiconductor polarities under different doping conditions. Before discussing the results in detail, it is worth noting that beyond the mechanisms discussed above, AgNO_3 treatment may also induce an additional removal of surface ligands (Figure S6, Supporting Information), which could modestly strengthen inter-NC coupling and influence charge transport. Nevertheless, the degree of ligand removal is limited, and, as elaborated in the following sections, the intricate structural, spectroscopic, and electrical variations observed in Ag^+ -treated InAs NC films cannot be rationalized solely by enhanced inter-NC electronic coupling.

XPS measurements were conducted to examine the changes in binding characteristics of the elements in InAs NCs through Ag^+ doping. For the *n*-type InAs NCs, there was no significant alteration in the shape and position of the In 3d and As 3d peaks after doping, resulting in an Ag/As ratio of 14% (Figure 2a,b). Of course, the Zn 2p peak was absent both before and after doping (Figure 2c), whereas the Ag 3d peak emerged after doping (Figure 2d). Moreover, there was no notable change in the atomic compositional ratio between In and As throughout the process (In/As ratio from XPS analysis was 109% and 112% before and after doping, respectively). These findings indicate that Ag^+ does not substitute In in the lattice structure of the NCs. Therefore, the possibility of Case 2 can be dismissed under the given doping conditions for *n*-type InAs NCs. Instead, Ag^+ is likely to occupy interstitial sites within the lattice or reside on the NC surface, leading to an opposite doping effect. Based on the observations in Figure 1d, it is inferred that interstitial doping (Case 1) exerts a more significant influence. It is worth noting that the

electrical properties of the FETs remained unchanged even after thorough sonication of the NC thin films with fresh acetonitrile multiple times (Figure 2e), applied to eliminate any Ag^+ bound to the NC surface. This suggests that not a significant amount of Ag^+ is adsorbed onto the *n*-type InAs NCs under the given doping conditions. Additional experimental evidence supporting this hypothesis comes from grazing incidence X-ray diffraction (GIXRD) analysis, which can detect lattice distortions induced by Ag^+ doping. As shown in Figure 2f, Ag^+ doping on the InAs NCs resulted in a positive shift in the diffraction peak position (the peak originally at 25.72° shifted to 25.85° after Ag^+ doping), indicating lattice contraction (according to Bragg's law, the observed peak shift implies a reduction in the lattice constant of InAs from 6.00 Å to 5.96 Å after Ag^+ doping). Structural parameters estimated from the GIXRD data are summarized in Table 1. Considering that substituting In (tetrahedral covalent radius = 1.44 Å) with Ag (tetrahedral covalent radius = 1.52 Å) would typically expand the lattice, and that Ag^+ binding to the NC surface would not affect the crystal structure, Case 2 and Case 3 can be ruled out. Instead, we attribute the observed lattice contraction to the incorporation of Ag^+ into the interstitial sites within the InAs NC lattice.^[31] It is noteworthy that a similar contraction of the host crystal structure upon introduction of heteroatoms into the interstitial sites of the lattice has been also observed in Co-doped TiO_2 nanorods^[32] and Li-doped WO_3 .^[33] In addition, the broadness of the diffraction peaks is slightly increased with Ag^+ doping, but not as much to alter the NC dimension estimated from the Scherrer equation. These results

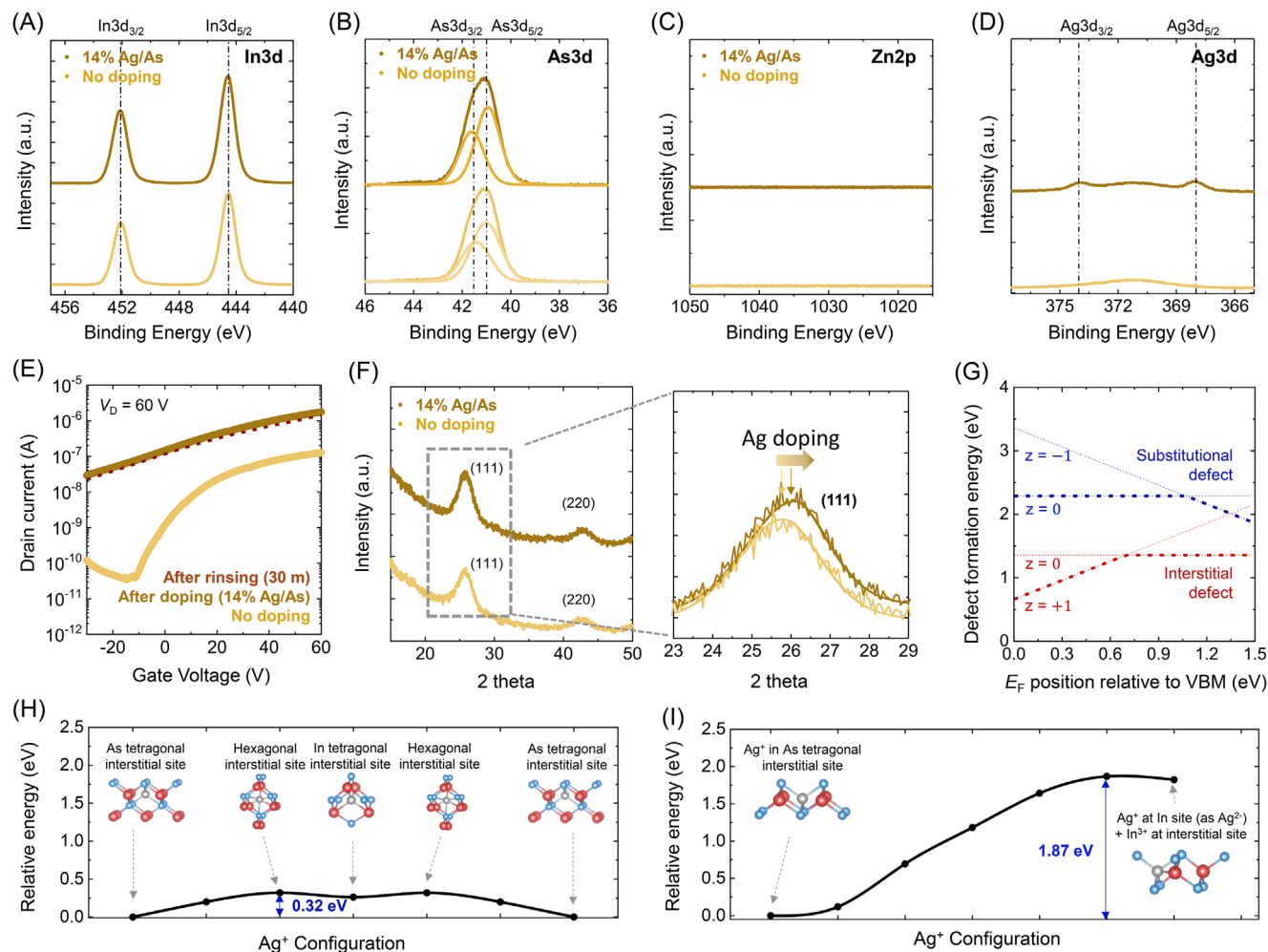


Figure 2. High-resolution XPS spectra of a) In 3d, b) As 3d, c) Zn 2p, and d) Ag 3d regions for *n*-type InAs NC films before and after Ag⁺ doping (Ag/As = 14%). e) Transfer characteristics of FETs based on *n*-type InAs NC films before and after Ag⁺ doping (Ag/As = 14%) and after rigorous rinsing (30 min). f) X-ray diffractograms of *n*-type InAs NC films before and after Ag⁺ doping (Ag/As = 14%). g) Formation energies of Ag-related defects in InAs NCs with varying E_F positions (the E_F position for the InAs NCs is depicted relative to the VBM position). Calculations were performed for an InAs lattice containing 79 In and 80 As atoms. The red and blue lines correspond to the formation energies of interstitial Ag⁺ defects within the lattice and substitutional Ag⁺ defects replacing In, respectively. h) Relative energy changes along the migration pathway of Ag⁺ between adjacent tetrahedral interstitial sites coordinated by As atoms. i) Relative energy changes along a pathway in which Ag⁺ replaces an In atom, displacing In³⁺ into a neighboring interstitial site.

suggest that the doping mechanism proceeds without significant size evolution of the InAs NCs.

We calculated defect formation energy using density functional theory (DFT) to investigate the potential introduction of Ag⁺ into interstitial sites within the InAs lattice, as shown in

Scheme 1a. The calculation details are provided in the Method. The results indicate that the formation energy of interstitial Ag defects (highlighted in red in Figure 2g) is consistently lower than that of substitutional Ag defects (highlighted in blue in Figure 2g), irrespective of the doping level of the InAs host (or

Table 1. Summary of the structural parameters estimated from XRD analysis of InAs NCs.

InAs NCs	Ag contents [%]	(111) peak position [°]	Lattice constant [Å]	(111) peak FWHM [°]	Crystal size [nm]
<i>n</i> -type	0	25.72	6.00	2.51	3.2
	14	25.85	5.96	2.54	3.2
<i>p</i> -type	0	25.79	5.98	2.57	2.6
	37	25.79	5.98	2.49	2.6
	85	26.12	5.90	2.49	2.6

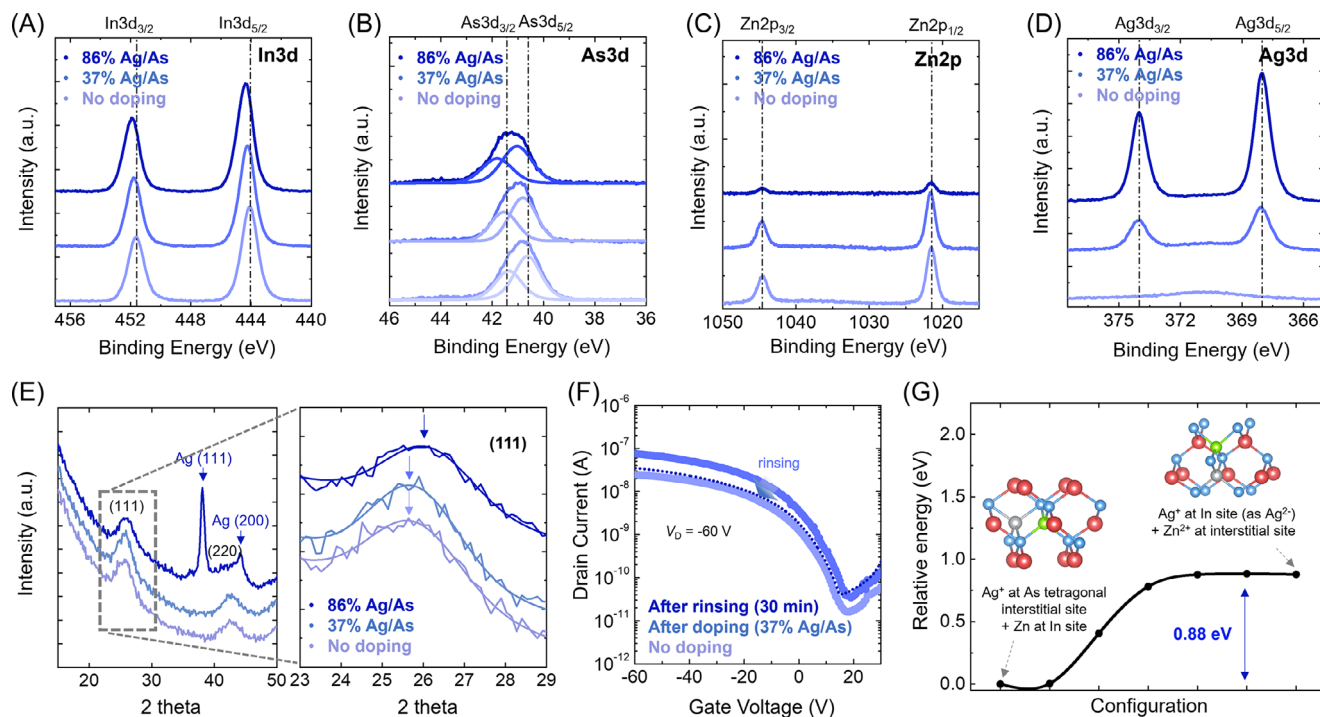


Figure 3. High-resolution XPS spectra of a) In 3d, b) As 3d, c) Zn 2p, and d) Ag 3d regions for *p*-type InAs NC films before and after Ag⁺ doping (Ag/As = 37% and 86%). e) X-ray diffractograms of *p*-type InAs NC films before and after Ag⁺ doping (Ag/As = 37% and 86%) f) Transfer characteristics of FETs based on *p*-type InAs NC films before and after Ag⁺ doping (Ag/As = 37%) and after rigorous rinsing (30 min). g) Relative energy changes along a pathway in which Ag⁺ ejects a Zn atom, ejecting Zn²⁺ into a nearby interstitial site.

the position of E_F). Considering that the incorporation of Ag⁺ into interstitial sites implies the potential for migration between such sites within the InAs lattice, we further calculated the energy barrier for Ag⁺ migration between adjacent tetrahedral interstitial sites. This calculation particularly focused on Ag⁺ surrounded by As atoms, which is anticipated to form the most stable interstitial configuration (Figure 2h). Along this migration pathway, Ag⁺ moves through a hexagonal interstitial site coordinated by both In and As atoms, as well as a tetrahedral site coordinated solely by In atoms. The calculated energy barrier for this migration is 0.32 eV, comparable to typical values for interstitial Ag transport in crystal lattices.³⁰ Additional DFT calculations were conducted to assess the potential for Ag⁺ (introduced into interstitial sites) to substitute In sites within the lattice, as illustrated in Scheme 1b. Beginning with a configuration where Ag⁺ occupies a tetrahedral interstitial site surrounded by As atoms, we examined the relative energy changes along a pathway in which Ag⁺ replaces an In atom, displacing In³⁺ into a nearby interstitial site (Figure 2i). The substitution process exhibits a calculated energy barrier of 1.87 eV, significantly higher than the 0.32 eV required for interstitial migration. This result indicates that Ag⁺ preferentially occupies interstitial sites rather than substituting for In atoms. Moreover, the reverse process—Ag⁺ migrating from a substitutional In site back to an interstitial site while the displaced In³⁺ returns to its original lattice position—features a very low energy barrier of only 0.05 eV (Figure 2i). This implies that even in cases of substitutional doping, Ag⁺ could easily escape and revert to an interstitial configuration. In summary, the DFT results affirm that interstitial doping of Ag⁺ (Scheme 1a) is significantly

more energetically favorable than substitutional doping (Scheme 1b).

In parallel with the complex electrical characteristics shown in Figure 1h,i, intricate results were obtained from XPS analysis of *p*-type InAs NC films doped with Ag⁺ (Figure 3a–d). Under low doping conditions (Ag/As ratio of 37%), corresponding to a situation where Ag⁺ exhibited a *p*-type doping effect from electrical measurements, the XPS spectrum revealed a slight positive shift in binding energies for In 3d and As 3d peaks, while the Zn 2p peak remained nearly constant. These findings were accompanied by the emergence of an Ag 3d peak, indicating the presence of Ag⁺ within the NC films. Despite the presence of Ag⁺, no significant alteration in the atomic compositional ratio between In and As or In and Zn was observed. Additionally, a marginal shift in the (111) peak position was noted from XRD analysis (Figure 3e). The (111) diffraction peak of the *p*-type InAs NCs before and after Ag⁺ doping was situated at 25.79° (corresponding lattice constant = 5.98 Å), indicating no substantial expansion or contraction within the lattice due to Ag⁺ doping. These results collectively imply that the introduction of Ag⁺ (at low concentrations) into the *p*-type InAs NC films slightly altered the local chemical environment of In and As but not the lattice structure itself as significantly as it did for the *n*-type InAs NC film.^[34–36] Hence, it is hypothesized that the majority of Ag⁺ is adsorbed on the surface of InAs NCs (Case 3 or 3') rather than being integrated into the InAs lattice (Case 1 or Case 2/2'). Unlike the *n*-type InAs NCs, the preferential surface adsorption of Ag⁺ in the *p*-type NCs under similar doping conditions is likely associated with the presence of Zn on their surfaces. As reported in our

previous work,^[9] a significant fraction of Zn introduced during the synthesis of *p*-type InAs NCs resides at the NC surface. This surface-localized Zn appears to modify the preferred pathway for Ag⁺ incorporation, acting as a barrier that suppresses the penetration of Ag⁺ ions into the lattice and thereby limiting the formation of interstitial Ag⁺ dopants at low doping concentrations. Since the quantity of Zn remains constant under this Ag⁺ doping condition (Ag/As ratio of 37%), it is proposed that Ag⁺ is physically adsorbed at the vacant sites of InAs NC surface, without displacing the pre-existing Zn on the surface (Scheme 1g). Consequently, the enhanced *p*-type effect observed with Ag⁺ doping under this condition in the *p*-type InAs NC film from FET measurements is attributed to the surface dipole generated by Ag⁺ adsorbed on the NC surface. Given that the binding of Ag⁺ on the NC surface is weaker than that of Ag⁺ incorporated within the lattice, thorough rinsing of the NC film can eliminate Ag⁺ from the NC surface. Figure 3f compares the transfer characteristics of FETs based on Ag⁺-doped *p*-type InAs NC films before and after rigorous sonication of the film using fresh acetonitrile for 30 min. Unlike the strong *n*-doping effect observed in FETs based on Ag⁺-doped *n*-type InAs NC films (Figure 2e), the *p*-type doping effect on *p*-type InAs NC films vanished upon rinsing. This further supports the notion that Ag⁺ is deposited on the surface of *p*-type InAs NCs under the specified doping condition.

At higher doping condition (Ag/As ratio of 86%), corresponding to the complete conversion in the semiconductor polarity as shown in Figure 1i, the peak positions of In 3d and As 3d in the XPS spectrum further shifted to higher binding energies, indicating a significant change in the chemical environment around In and As.^[9,37] Additionally, the (111) peak position from the X-ray diffractogram shifted to higher 2 theta values (Figure 3e). The (111) diffraction peak of the *p*-type InAs NCs, originally at 25.79° (corresponding lattice constant = 5.98 Å), remained constant under low Ag⁺ doping conditions (Ag/As ratio of 37%). However, at high Ag⁺ doping condition (Ag/As ratio of 86%), the peak shifted to 26.12° (corresponding lattice constant = 5.90 Å), indicating a substantial contraction in the lattice, consistent with the results shown in Figure 3e. The lattice contraction suggests that Ag⁺ is incorporated into the interstitial sites of the InAs lattice (i.e., Case 1). If Ag⁺ were incorporated into the substitutional sites (either In or Zn), it would result in lattice expansion, given that Ag has a larger tetrahedral covalent radius (1.52 Å) than In (=1.44 Å) or Zn (= 1.31 Å).^[31] Therefore, Scheme 1d would be a more suitable scenario at the given Ag⁺ doping condition than Scheme 1e,f. In this scenario, Ag⁺ acts as an *n*-type dopant in the host InAs NCs, lowering the CBM and VBM and bringing the CBM closer to *E_F*. This mechanism explains how the initially *p*-type InAs NC films exhibit *n*-type characteristics at the high Ag⁺ doping condition (Ag/As ratio of 86%). In addition to the peak shift of the InAs (111) reflection, X-ray diffraction patterns at high doping concentrations revealed additional peaks at ~38° and ~44°, which can be assigned to the (111) and (200) planes of metallic silver, respectively. We attribute the appearance of these peaks to the partial reduction of excess Ag⁺ ions introduced under high doping conditions, leading to the nucleation of metallic Ag domains (Figure S7, Supporting Information). Notably, these metallic Ag domains were more frequently observed in *p*-type InAs NCs than in *n*-type ones, which can be explained by the presence of surface

Zn atoms acting as a barrier that suppresses Ag⁺ incorporation into the InAs lattice.

Another significant observation from the XPS profile is the reduced intensity of the Zn 2p peak under the high Ag⁺ doping condition (compared to that under low Ag⁺ doping conditions), indicating that the introduction of Ag⁺ displaces Zn. Considering that Zn in *p*-type InAs NCs is present both within the lattice and on the surface, we examined how Ag⁺ doping affects Zn at each location separately. For the Zn bound to the surface, we anticipate that the excess NO₃⁻ introduced alongside Ag⁺ (remember that Ag⁺ is added to InAs NCs using AgNO₃ solution) under high doping conditions can release the Zn²⁺ ions physically adsorbed on the surface of *p*-type InAs NCs. This is likely due to the stronger Zn–NO₃ binding compared to Ag–NO₃ binding, promoting the formation of Zn(NO₃)₂ and its subsequent desorption from the surface. Hence, Scheme 1g represents a plausible scenario at the surface under the specified Ag⁺ doping condition. We predict that the substitution of Zn²⁺ with Ag⁺ on the surface of *p*-type InAs NCs would diminish the surface dipole-induced *p*-doping effect, as the surface dipole moment induced by Ag⁺ is expected to be smaller than that induced by Zn²⁺. Furthermore, once the surface Zn—which initially acted as a barrier to Ag⁺ diffusion—is partially replaced or removed, the penetration of Ag⁺ ions into the lattice becomes more favorable, leading to effective *n*-type doping at higher concentrations. It is noteworthy that the formation of interstitial defects of Ag on the InAs host is reduced as *E_F* approaches VBM (i.e., in more *p*-type doped InAs) (Figure 2g). This observation suggests that interstitial *n*-type doping with Ag⁺ is more favorable in *p*-type InAs than in *n*-type InAs. Overall, this replacement of Zn²⁺ at high doping concentration condition would consequently contribute to the *n*-type doping effect at this doping level.

On the other hand, the impact of Ag⁺ on Zn located within the InAs lattice was investigated using DFT calculations. In comparison to the high energy needed for Ag⁺ to substitute an In site in the pristine InAs lattice (1.87 eV; Figure 2i), the energy barrier for Ag⁺ replacing Zn in the Zn-doped InAs lattice is notably lower, calculated at 0.88 eV (Figure 3g). These findings suggest that Ag⁺ substitution at cationic sites is more favorable in the presence of Zn, indicating that substitutional doping is more likely in *p*-type InAs NCs containing Zn than in *n*-type InAs NCs without Zn. However, the substitutional energy barrier (0.88 eV) still remains significantly higher than the energy barrier for Ag⁺ migration between interstitial sites (0.32 eV), implying that while substitution may be more feasible in *p*-type NCs, interstitial doping still remains energetically more favorable overall. Furthermore, if Ag⁺ were to substitute Zn²⁺ (leading to a net negative potential), one would expect an increase in the *p*-type characteristics of the host material. However, this anticipated trend is not supported by the electrical characteristics observed under the specified doping conditions (Figure 1i). Collectively, these results substantiate the notion that Ag⁺ predominantly serves as an interstitial *n*-type dopant, elucidating the observed shift from *p*-type to *n*-type behavior in InAs NC films upon Ag⁺ doping.

3. Conclusion

In this study, we systematically investigated the effects of Ag⁺ doping on InAs NCs with distinct initial semiconductor

polarities. We found that Ag^+ doping leads to contrasting electronic outcomes based on the doping concentration and the host NC type. In *n*-type InAs NCs, Ag^+ consistently induces an *n*-type doping effect through interstitial incorporation, as supported by electrical measurements, spectroscopic analyses, and DFT calculations. In *p*-type InAs NCs (intrinsically doped with Zn during synthesis), low concentrations of Ag^+ exhibit *p*-type behavior through surface dipole formation, while higher concentrations reverse the polarity to *n*-type due to interstitial Ag^+ doping and partial surface Zn displacement. This detailed analysis emphasizes the crucial role of doping configuration—interstitial, substitutional, and surface—in determining semiconductor polarity. Our results provide a flexible approach for post-synthetic control of charge carrier type in colloidal III–V NCs, enhancing their potential for high-performance optoelectronic devices.

4. Materials and Methods

Materials: For *p*-type InAs NCs, InCl_3 (98%, Sigma–Aldrich), DMA-As (99%, Strem), Et_2Zn solution (1 M in hexane, Sigma–Aldrich), tri-octylphosphine (TOP, 97%, Uniam), and anhydrous solvents (hexane, toluene, and 1-butanol, Sigma–Aldrich) were used without further purification. OLA (technical grade, 70%, Sigma–Aldrich) was purified by distillation and stored in a glove box. For *n*-type InAs NCs, InCl (99.999%, Sigma–Aldrich) and OLA (>98%, Sigma–Aldrich) were used without further purification. For the solid-state ligand exchange step, EDT (98%, Sigma–Aldrich) and acetonitrile (anhydrous, 99.8%, Sigma–Aldrich) were used without further purification. For the solid-state doping step, AgNO_3 (99.0%, Sigma–Aldrich) and acetonitrile (anhydrous, 99.8%, Sigma–Aldrich) were used without further purification. For FETs, a heavily doped Si wafer (n^{++} , <0.005 Ωcm) with a thermally grown SiO_2 layer (300 nm) (Namkang Hi-Tech) was used as the substrate. For XPS measurement, a bare Si wafer (Namkang Hi-tech) was used as a substrate.

Synthesis of *n*-Type InAs NCs: *n*-type InAs NCs were synthesized following a method similar to that described by Ginterseder et al.^[28] In a three-neck round-bottom flask, 1.5 mmol of InCl was dissolved in 7.2 mL of OLA, and the mixture was degassed at 60 °C for 30 min. After purging the atmosphere with nitrogen, 0.3 mL of TOP was added, and the reaction mixture was then heated to 270 °C. Separately, 0.8 mmol of DMA-As in 2 mL of OLA was heated to 50 °C for 5 min inside a glove box. Once the indium mixture reached the reaction temperature, 1.3 mL of the resulting As precursor solution was injected into the reaction flask containing the indium precursor solution under vigorous stirring. After a 60-min reaction, the flask was cooled to room temperature. The InAs NCs were obtained by centrifugation using a hexane/1-butanol mixture. The NCs were then redispersed in toluene for further applications.

Synthesis of *p*-Type InAs NCs: *p*-type InAs NCs were synthesized following a modified method similar to that reported by Yoon et al.^[9] The In precursor solution was prepared by degassing 0.5 mmol of InCl_3 dissolved in 8 mL of OLA at 120 °C for 30 min. For the As precursor solution, 0.6 mmol of DMA-As and 0.8 mL of OLA were mixed under a nitrogen atmosphere. After stirring for 10 min, 0.5 mL of TOP and 0.6 mL of Et_2Zn solution were added. The mixture was heated to 240 °C and maintained for 10 min, then cooled down. The As precursor was added to the In precursor at room temperature under nitrogen, and the mixture was heated and maintained at 160 °C for 10 min to initiate seed formation. The temperature was then ramped to 320 °C over 20 min. During growth, additional In and As precursors were continuously injected ($\text{In/As} = 0.8$, injection rate = 0.1 mL min^{-1}). While maintaining the reaction temperature at 320 °C, pulsed precursor injection was applied (5 min injection / 5 min delay; average injection rate = 0.1 mL min^{-1}). The resulting NCs were purified using hexane and 1-butanol in a nitrogen-filled glovebox. The NCs were then redispersed in toluene for further use.

FET Fabrication: Cr/Au (5/50 nm) electrodes were thermally deposited using a shadow mask onto a heavily *n*-doped Si substrate with

a 300 nm thick thermally grown SiO_2 layer. InAs NCs dispersed in toluene (10 mg mL^{-1}) were spin-coated at 2000 rpm for 30 s, which yielded NC films with thickness ≈ 30 nm. For ligand exchange, the NC films were treated with 50 mM EDT in acetonitrile for 60 s and then rinsed twice with fresh acetonitrile. For Ag^+ doping, the resulting ligand-exchanged NC films were treated with a specific Ag concentration in acetonitrile for 60 s and then rinsed twice with fresh acetonitrile, followed by annealing at 220 °C for 30 min.

Characterization: UV-Vis-NIR absorbance spectra of *p*- and *n*-type InAs NCs were obtained using a V-770 (JASCO) spectrophotometer, and the films were deposited on a glass substrate. XPS measurements were conducted on films deposited on a Si substrate coated with a Cr/Au (5/50 nm) layer. The binding energies were calibrated based on the C1s core level (284.8 eV). Ambient-pressure PYS measurements for films of *p*- and *n*-type InAs NCs were performed using an APS04 system (KP Technology). STEM samples were prepared on 400-mesh Cu grids and imaged using a JEM-ARM200CF (JEOL) at 200 kV. Electrical characterization of the resulting devices was performed within a vacuum probe station (MSTECH M5VC) connected to a Keithley 4200-SCS parameter analyzer. GIXRD measurements at the 5D beamline of Pohang Light Source-II (PLS-II), Pohang Accelerator Laboratory, using 9.987 keV photon energy. The incident angle was fixed at 0.4, just above the critical angle of each sample. The focused beam size at the sample position was 1.5 mm (H) $\times$ 0.5 mm (V). Samples were mounted on a computer-controlled translation stage to enable precise alignment. The GIXRD patterns were fitted using the LIPRAS software.

Simulation: DFT calculations were conducted to examine the stability of Ag defects in InAs NCs. The electron–ion interaction was described by the Projector Augmented Wave method,^[38] as implemented in the Vienna Ab initio Simulation Package.^[39] The exchange–correlation energy was evaluated using the HSE06 hybrid functional proposed by Heyd, Scuseria, and Ernzerhof.^[40] The energy cutoff for the plane waves was set to 276.7 eV. A cubic supercell containing 64 atoms was used, and the Brillouin zone was sampled using a $3 \times 3 \times 3$ Monkhorst–Pack grid. Migration barrier energy of defects was obtained by using the climbing nudged elastic band method.^[41]

For the formation energy of Ag defects in InAs NCs, we utilized an exchange–correlation functional proposed by Perdew, Burke, and Ernzerhof.^[42] We employed a previously developed InAs NC model.^[9] The defect formation energy of a defect *D* was calculated as $E_f(D^q) = E_{\text{tot}}(D^q) - E_{\text{tot}}(0) - \sum_i n_i \cdot \mu_i + q(E_F + E_{\text{VBM}}) + E_{\text{corr}}$, where $E_{\text{tot}}(D^q)$ and $E_{\text{tot}}(0)$ are the total energies of an NC with and without a defect *D* in charge state *q*, respectively, n_i is the number of atomic species *i* added to form the defect, μ_i is the corresponding chemical potential, and E_{corr} is the correction term for the charged defects, which was obtained by following a scheme proposed by Freysoldt, Neugebauer, and Van de Walle.^[43] The formation energies were obtained under an Ag-rich and In-poor condition.

Statistical Analysis: All the average and standard deviation values are obtained from more than five samples.

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

doping, InAs nanocrystals, interstitial doping, semiconductor polarity, surface doping

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