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Introduction

Photodetectors, which convert optical signals into electrical signals, are essential elements applied in high-resolution imaging techniques, light wave communications, and optical interconnects.¹ Most of recent academic attention has been focused on the development of photodetectors with a minimum thickness for the maximum photon absorption, targeting cost-effective, and superior detector performance, spanning across the broad wavelength regions.^{2,3} Various nanostructures, especially 1D semiconductor materials, including nanowires, nanorods and so forth have been extensively engineered to generate a significant amount of surface states for carrier charge trapping, and extending the photocurrent lifetimes and photoresponse speed.^{4–9} However, large-scale inte-

Broad-band three dimensional nanocave ZnO thin film photodetectors enhanced by Au surface plasmon resonance[†]

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ZnO semiconductor films with periodic 3D nanocave patterns were fabricated by the thermal nanoimprinting technology, which is promising for photodetectors with enhanced light harvesting capability. The Au nanoparticles were further introduced into the ZnO films, which boosts the UV response of ZnO films and extends the photodetection to visible regions. The best UV photoresponse was detected on the 3D nanocave ZnO–Au hybrid films, attributing to the light trapping mechanism of 3D periodic structures and the driving force of the Schottky barrier at the ZnO/Au interface, while the high visible photoresponse of ZnO–Au hybrid films mainly results from the hot electron generation and injection process over the Schottky junctions mediated by Au surface plasmon resonances. The work provides a cost-effective pathway to develop large-scale periodic 3D nanopatterned thin film photodetectors and is promising for the future deployment of high performance optoelectronic devices.

> gration of the semiconductor 1D nanostructures for highperformance electronic devices requires elaborate and costly methods, such as flow-assisted alignment,¹⁰ Langmuir– Blodgett,¹¹ electric-field-directed assembly,¹² contact printing,¹³ *etc.* Moreover, the above assembled nanowires have limited light capturing capability, which is of significant importance to engineer the interplay between photons and optoelectronic materials and devices at micro- and nanoscopic scales.

> The 3D nanostructures, such as nanocones,¹⁴ nanocavity,¹⁵ nanowell¹⁶ structures and so forth were reported to possess unique light management properties.17 Theoretically, the absorption of 3D nanostructures can reach up to the Lambertian limit of $4n^2$ (*n* denotes the refractive index), which could further benefit photodetectors by achieving higher quantum efficiency. Therefore, it is of significant importance to develop a cost-effective and large-scale method to fabricate various 3D periodic nanostructures with different light trapping mechanisms for high performance photodetectors. Additionally, metal localized surface plasmonic resonance (LSPR) has been reported to be an efficient way to focus light into a nanometerscale due to the localized and intensified electromagnetic field.^{18,19} The plasmonic nanostructures can also directly convert the harvested light into electrical energy by generation of so-called "hot electrons", 20,21 which is an efficient way to broaden the photoresponse frequency of photodetectors.

> In our work, ZnO was employed as a representative semiconductor material due to its unique optical and electrical pro-

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perties for ultraviolet (UV) photodetector applications. The 3D nanocave ZnO films were firstly patterned by the direct thermal nanoimprinting lithography, which has been demonstrated as a cost-effective method for large-scale patterning of micro/nano-structures.^{22–24} Subsequently, Au nanoparticles were introduced into the semiconductor films with the aim of enhancing the photoresponse of ZnO films. The patterned ZnO–Au hybrid film represents superior photoresponse performance in both UV and visible regions due to the driving force of the Schottky barrier at the semiconductor/metal interface and the improved light harvesting capability achieved by the 3D photonic mode and Au LSPR.

Experimental

Preparation of ZnO and ZnO–Au precursor sol films on Si/SiO₂ wafer

ZnO precursor films were prepared by a sol-gel procedure, where the zinc acetate dihydrate $(Zn(CH_3COO)_2 \cdot 2H_2O)$ was used as a precursor, *N*,*N*-dimethylformamide (DMF) as solvent and Diethanolamine (DEA) as a stabilizer. Typically, 0.05 mol zinc acetate dihydrate was firstly dissolved in 100 ml of DMF, followed by continued stirring at room temperature. During this period, 0.05 mol DEA was added dropwise into the solution until the solution showed a clear and homogeneous polymeric aqueous ZnO precursor solution.

The Au sol was prepared by dissolving 3 mg chloroauric acid trihydrate into 30 ml DMF at 80 °C for 1 h. The PH of the solution was adjusted to 10 to obtain the Au sol under continuous stirring. The ZnO-Au precursor sol was obtained by mixing 2 ml Au sol (0.049 mg ml⁻¹) and 8 ml ZnO sol (65.112 mg ml⁻¹) by ultrasonic treatment for 5 min.

The SiO₂ (200 nm)/Si wafers were first ultrasonically cleaned in a mixture solution of $NH_3 \cdot H_2O$, H_2O_2 and deionized water (1:1:5 in volume) for 15 min, followed by ultrasonic rinsing in deionized water for 5 min and blow drying by pressurized nitrogen gas. Then, a series of thin-films of around 150 nm were subsequently formed by spin coating the asobtained sols (ZnO and ZnO–Au) on SiO₂/Si wafers at a speed of 1000 rpm for 10 s followed by 4000 rpm for 20 s.

Nanopatterned film by nanoimprinting lithography

Surface-patterned 3D nanocave ZnO thin films (P-ZnO) were realized by direct imprinting on a polymeric ZnO precursor sol and subsequent annealing process. The polydimethylsiloxane (PDMS) soft stamps were used to pattern the sol films. The PDMS stamps were prepared by casting a 10:1 weight ratio mixture of a basic agent and a firming agent on the pre-patterned Si master mold and substantially curing at 60 °C for 3 h. The patterned PDMS was then attached onto the obtained sol films, followed by the thermal nanoimprinting process (NC-AX1401, Nanocarve) under 0.17 MPa and 150 °C for 2 h until the sols were transferred to the stable nanopatterned gels. The procedure was schemed as shown in Fig. 1a. After the imprinting process, the ZnO-gel patterns were crystallized



Fig. 1 (a) Schematic procedure of the direct ZnO patterning process by nanoimprinting lithography. The SEM images of (b1) the tilted cross section view of flat ZnO films formed by spin coating, (b2) top view of patterned ZnO and (b3) ZnO–Au films. (c1) The XRD patterns of ZnO and ZnO–Au films. The AFM image of (c2) patterned ZnO film and (c3) patterned ZnO–Au films.

under 500 °C for 1 h under ambient atmosphere. The same procedure was applied to obtain the patterned ZnO–Au thin films (labeled as P-ZnO–Au) on Si/SiO₂ wafers. For control experiments, flat ZnO and ZnO–Au thin films were fabricated in the same way without the nanoimprinting process.

Physical and optoelectronic characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku Dmax X-ray diffractometer using Cu Ka radiation. The morphologies of ZnO and Au nanoparticles as well as the ZnO based thin films were characterized by using a scanning electron microscope (SEM, Hitachi S-4800), transmission electron microscopy (TEM, JEM-2010F), and atomic force microscopy (AFM, Bruker Dimension Icon, tapping mode). An Energy Dispersive Spectrometer (EDS) was employed to estimate the element contents. The absorption spectra of ZnO-Au sol and ZnO based thin films were recorded by using a standard UV-vis spectrometer (Agilent Cary 5000). Optoelectronic measurements were carried out on a semiconductor characterization system (Agilent B1500A) by depositing a pair of 10 nm/ 800 nm Ti/Au electrodes with a channel length of 500 µm, where light illuminations were performed by using the UV lamps (3 mW cm⁻²@254 nm and 3 mW cm⁻²@365 nm) and a Xe lamp (PLS-SXE300UV) coupled with visible narrow band filters (450, 520 and 600 nm). All measurements were performed in air and at room temperature. The electromagnetic simulations were accomplished by employing the finite difference time domain (FDTD) method. A plane wave light source was irradiated normally to the devices. The source was set to be polarized along the x-axis considering that the hexagonal arranged structure of ZnO is polarization independent. The unit cell of the patterned structure was set as the simulation region using anti-symmetrical boundaries in the x-axis, symmetrical boundaries in the *y*-axis and perfectly matched layer (PML) boundaries in the *z*-axis. Optical Constants of ZnO were from ref. 25.

Results and discussion

Fig. 1b represents the SEM images on Si/SiO₂ wafers for each step during the imprinting process. The tilted cross section view of the ZnO thin film in Fig. 1b1 indicates the uniform coating with a thickness of about 150 nm. Fig. 1b2 and b3 show the top view SEM images of patterned ZnO and ZnO-Au films, respectively. The uniform and periodic patterns indicate the large scale patterning capability of the nanoimprinting process. Due to the small disposal amount of Au nanoparticles, only a few small Au nanoparticles can be found on the surface of the patterns and some of them were encapsulated in the ZnO environments. EDS was used to estimate the Au content in the hybrid ZnO-Au films (Fig. S1⁺), which showed that the mass ratio of Au: Zn was around 1:250. Although the EDS result is not as accurate as characterizing the element contents, the mass ratio of Au: Zn suggests the very dilute Au nanoparticles by ZnO. The cross sectional view of the patterned thin film is shown in Fig. S2a.† The patterned film possesses a little thicker film thickness of 155 nm than the flat film of 150 nm due to the imprinted nanotextures. The depth of the nanocave is 41 nm. To confirm the pattern structures, AFM measurements were then conducted on the patterned ZnO and ZnO-Au films, as indicated in Fig. 1c2 and c3, respectively. The corresponding profile curves are shown in Fig. S3.[†] Both the ZnO and ZnO-Au patterns were found to possess a diameter of ca. 750 nm, height of ca. 40 nm and pitch of 1 µm.

The crystallization of ZnO and ZnO-Au films was then characterized by XRD, as shown in Fig. 1c1. Three main diffraction peaks in the XRD patterns can be indexed to the (100), (002) and (101) planes of crystallized ZnO, revealing a hexagonal wurtzite structure (Zincite, JCPDS 36-1451) for both the films. For the ZnO-Au films, the diffraction peaks centered at 37.85° and 44.03° correspond well with the (111) and (200) planes of face-centered cubic Au. The crystallite sizes of Au and ZnO are calculated to be 31.5 nm and 50 nm, respectively, according to the Scherrer equation. The representative TEM and HRTEM images of ZnO and Au are indicated in Fig. S4-S6.† The mean size of ellipsoidal ZnO nanoparticles is estimated to be ca. 65 nm. Most of the Au nanoparticles are spherical and the particle size is distributed from 20 to 41 nm with a mean particle size of 29.7 nm. The HRTEM images of ZnO in Fig. S4b[†] and Au in Fig. S6[†] indicate good crystallinity from the well-defined fringes at 0.249 nm from the ZnO (101) plane and 0.241 nm from the Au (111) plane, which matches well with the corresponding XRD results.

The ZnO film-based photodetector was then constructed by depositing a pair of 10 nm/800 nm Ti/Au electrodes with a channel length of 500 μ m, as illustrated in Fig. 2a. The linear current–voltage (*I–V*) curves on the four different devices in



Fig. 2 (a) Schematic illustration of ZnO film based photodetectors. I-V curves of different devices under (b) dark conditions and (c) 254 nm and (d) 365 nm illuminations.

Fig. 2b-d suggest good ohmic contact between ZnO films and the Ti/Au electrodes. Fig. 2b shows the dark current of all devices. The flat ZnO film is highly resistive under dark conditions due to the low-conductivity depletion layer near the surface governed by surface oxygen adsorption/desorption. The P-ZnO shows a little higher dark current, compared with the ZnO films, possibly due to the increased surface area. With the deposition of Au nanoparticles (NPs), the dark currents for both the ZnO-Au and P-ZnO-Au were found to decrease due to the possible formation of a Schottky junction at the interface of Au NPs and ZnO thin films.²⁶ The work function of ZnO (4.45 eV) is lower than that of the metal Au (5.1 eV). Under thermal equilibrium, the electrons from the conduction band of the ZnO layer move towards the Au NPs, resulting in the downward band bending of energy levels, and hence forming a space charge region (Schottky barrier) at the ZnO-Au interface.²⁷ The loss of electrons from the conduction band of the ZnO results in a decrease of dark currents for the ZnO-Au and P-ZnO-Au photodetectors. The P-ZnO-Au shows a little higher dark current than the ZnO-Au due to the surface patterns.

Fig. 2c and d show the photocurrents of the above four photodetectors under 254 and 365 nm light illuminations, respectively. The significantly increased currents under both 254 and 365 nm UV illuminations indicate clearly a UV sensitive photoconduction of all the ZnO based photodetector devices. The photoresponse of the devices under 365 nm irradiation is slightly lower than that under 254 nm. The photoconductive mechanism of ZnO films under UV illuminations generally includes the photogeneration of free carriers and the electrical transport through the thin films.²⁸ The generated electron–hole pairs under UV light result in reduction in the depletion barrier thickness and an increase in the free carrier concentration. With respect to the conventional flat ZnO film, the photocurrent of P-ZnO films is found to be ~14

times as high as that for the flat ZnO films under 254 nm illumination, attributing to the effective photon capturing properties of the 3D periodic nanocave patterns. Additionally, a larger surface-to-volume ratio of the patterned films may endow more carriers in three dimensions and in turn the increased photocurrent.

The absorption spectra of all the samples were recorded to understand the photodetection origin, as shown in Fig. S7.† All the samples show the periodic peaks, due to the interference effects. The P-ZnO and P-ZnO-Au films show some absorption enhancement at the interference peaks. However, due to the very thin ZnO film thickness, the incident light (even for the UV region) could not be absolutely absorbed by the ZnO layer, which would be reflected back toward the incident space or absorbed by the Si substrate. The problem would be more significant in the conventional nanowire photodetectors without a light trapping strategy.²⁹ As a result, the obtained overall absorption spectra cannot reflect the real absorbance of ZnO layers. In order to visualize the light capturing properties of the 3D periodic structure, FDTD simulations are then performed on both the flat and patterned ZnO films. Fig. 3 presents the distributions of electric field $(|E|^2)$ under 254 and 365 nm illuminations. In the case of the flat ZnO films (Fig. 3a1 and b1), interference fringes along the z direction are obviously observed due to the vertical light reflection. Fig. 3a1 and b1 present the distributions of electric field $(|E|^2)$ in planar films under 254 and 365 nm illuminations. Only interference fringes along the z direction (normal direction) are observed, which indicates that the electric field cannot be effectively confined within the absorbing layer, and most of the incident light passes through the oxide layer. In the case of patterned ZnO films, the interference along the x direction, due to the lattice scattering effect, is also identified in addition to the interference along the z direction as observed in Fig. 3a2 and b2. Usually, the constructive interference along the x direction is called as the Bloch modes.³⁰ Since the periodicity of the ZnO pattern is much larger than the incident wavelength, the number of interference fringes along the xdirection is quite big. It can be clearly seen that the incident light is more strongly trapped in the periodical nanopatterned



Fig. 3 The electric field profiles in (a1, b1) flat ZnO films and (a2, b2) surface-patterned nanocave ZnO films under (a1, a2) 254 nm and (b1, b2) 365 nm irradiations.

ZnO films compared to the flat ZnO film because of the hybrid interference. Moreover, the trapping of light under 254 nm illumination (Fig. 3a2) is stronger than that under 365 nm (Fig. 3b2), which could account for the variation of the photoconductive performance as illustrated in Fig. 2c and d.

For the ZnO-Au hybrid films, the photocurrents of ZnO-Au and P-ZnO-Au are increased significantly when compared with that of the ZnO films, which may be attributed to the driving force of the Schottky barrier at the ZnO/Au interface. The local Schottky contact points at the ZnO/Au interface improve the surface band bending, leading to a stronger surface electric field compared to the ZnO. Under UV illumination, photo-generated holes move to the surface through the built-up surface electric field, leading to electron-hole spatial separation and thus the decreased possibility for electron-hole recombination.³¹ More photogenerated electrons could be extracted to the outer electrode on ZnO-Au hybrid devices, contributing to an increase in the photocurrent under UV illumination. The P-ZnO-Au shows the highest photocurrent with 26 times enhancement compared to that of the flat ZnO films, which is resulted from the co-contribution of the 3D patterned light management structure and ZnO/Au interface.

The transient currents of the above four different photodetectors are also conducted under the bias voltage of 5 V (Fig. 4a), which corresponds well with the *I*-V results. The corresponding photocurrent (I_{on}) and photo-dark current ratio (I_{on}/I_{off}) values are summarized in Fig. 4b. The I_{on}/I_{off} values of the ZnO–Au and P-ZnO–Au films are significantly higher than that of the flat ZnO and P-ZnO films, respectively, originating from the smaller dark currents and higher photocurrents induced by the Schottky junction at the ZnO/Au interface, as discussed above. The best response (I_{on}/I_{off} value of 9478) is observed on P-ZnO–Au films with 19 times enhancement than that of the flat ZnO films.

Additionally, the flat ZnO films are found to possess the longest response time (both rise time and decay time), due to the slow electron-hole generation and recombination mediated by deep defect levels. It takes 118 s to reach the maximum current with a fall time (the duration that current reduces down to 10% of the maximum value as UV light is turned off) of 215 s. A little quicker response was observed as the surface film was patterned. It is expected that an increased surface area of the ZnO film would increase the recovery time due to the gas absorption. Abou Chaaya *et al.*³² found that the



Fig. 4 (a) The transient photoresponse. (b) The I_{on} and I_{on}/I_{off} values of all the devices under 254 nm irradiation. (c) Cycling test of P-ZnO-Au devices under 254 nm irradiation and a bias voltage of 5 V.

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response time firstly increases and then decreases with the increased surface area. Thus the response time of ZnO is much complicated which is significantly influenced by a number of factors such as the defect concentration, film thickness, crystallographic orientation, grain size and processing conditions, besides the surface area.^{32,33} The best response speed was observed on the P-ZnO-Au device. The rise and fall time are substantially decreased down to 24 and 15 s, respectively, which may be related with the efficient electron-hole separation and collection, as discussed above. The 6000 s cycling test was then conducted on the P-ZnO-Au film based photodetector to test the photostability. The photocurrent after the 6000 s test was found to be 89% of the original maximum current. This decrease may be related to the well-known instability of ZnO under UV illumination,³² which may be further improved by optimizing the electrical properties and the crystallinity of ZnO.34

The visible responses for the four photodetectors are conducted under 450, 520, and 600 nm visible illuminations, as shown in Fig. 5a-c. The photoresponses of the ZnO-Au-based devices are obviously detected from 450 to 600 nm visible illuminations. The photocurrent and the $I_{\rm on}/I_{\rm off}$ values of the photodetectors are summarized in Fig. 5d-e. The ZnO film devices show a weak visible light photoresponse. It should be noted that the generation of the photocurrent response at excitation energy below the ZnO band gap (3.3 eV) could be attributed to the presence of structural defects such as anti-site oxide, Zn vacancy and oxygen vacancy.35 The P-ZnO film shows a little higher photocurrent compared with the ZnO films benefiting from the superior light harvesting capability, as indicated by the electric field profiles in Fig. 6a and b. With the presence of Au NPs in the ZnO films (ZnO-Au and P-ZnO-Au films), a significant photocurrent enhancement is disclosed under visible illuminations. The P-ZnO-Au films possess the



Fig. 5 *I*–*V* characteristics of four photodetectors under visible light illuminations: (a) 450 nm, (b) 520 nm, and (c) 600 nm. The (d) I_{on} and (e) I_{on}/I_{off} of four different photodetectors as a function of wavelength in the visible region.



Fig. 6 The electric field profiles of (a) ZnO films, (b) P-ZnO films and (c) ZnO-Au films under 520 nm illumination.

highest photocurrent with 6 times enhancement compared with that of the flat ZnO films under 520 nm irradiation. The $I_{\rm on}/I_{\rm off}$ values of ZnO–Au and P-ZnO–Au films are found to be significantly higher than the flat ZnO and P-ZnO films. It is worth noting that the $I_{\rm on}/I_{\rm off}$ value of the P-ZnO–Au films is smaller than that of ZnO–Au films and the best photoresponse $(I_{\rm on}/I_{\rm off}$ value of 546 under 520 nm illumination) is observed on the ZnO–Au films due to the higher dark value of P-ZnO–Au films compared with the ZnO–Au films.

The mechanism of visible photoresponse for ZnO-Au hybrid film devices is different from that under UV light. The UV response of ZnO-based films mainly results from the direct generation of electron-hole pairs in ZnO films, which, however, contribute little under visible illumination. It is reported that Au surface plasmons excited by incident radiation can decay nonradiatively and generate energetic electrons instead of re-emitting a photon, thus creating a distribution of "hot electrons" well above the Fermi energy of the metal.³⁶ Hot electrons with energy above the Schottky barrier at the metal-semiconductor interface are directly injected into the conduction band of the ZnO.²¹ Further, the Schottky barrier at the interface is also helpful to prevent them from traveling back to the Au NPs. This plasmonic effect results in generation of enhanced photocurrent at photon energies below the band gap of the semiconductor and confers widened optoelectronic features to the metal-semiconductor hybrid device.

The absorption spectrum of the ZnO-Au sol was provided to show the Au plasmonic effect in Fig. S8,† where a broadband absorption peak centered at 534 nm is clearly observed. It means that the surface plasmon resonance could be excited in this visible range that would contribute to the hot electron injection process. The plasmonic effect could be further controlled by tuning the Au properties, as discussed in the literature.³⁷ In order to visualize the Au hot electron generation and injection process, FDTD simulations are performed to calculate electric field distribution across the ZnO-Au interface under 520 nm, as shown in Fig. 6c. The simulation is simplified by an Au nanoparticle with a diameter of 30 nm embedded in the ZnO film, according to the above XRD and TEM results. The color index represents the magnitude of the electric field intensity normalized with that of the light propagating in free space. The electric field intensity of pristine ZnO is very weak under 520 nm. By coupling the Au plasmonic structure, high electric field intensity can be found at the ZnO-Au interfaces, contributing to the hot electron generation

and injection process. These results indicate that the incorporation of Au nanoparticles is responsible for the extended visible response of ZnO–Au photodetectors.

Conclusions

In conclusion, we have constructed periodic 3D nanocave ZnO films by a cost-effective thermal nanoimprinting process for photodetector application. The 3D patterns delivered enhanced UV response, thanks to their efficient light trapping properties. The Au nanoparticles are further introduced into the ZnO film, which is found to boost the UV responsivity and extend the photodetection to the visible light region. The 3D nanocave ZnO-Au hybrid films show the best photoresponse and the fastest response time under UV regions, attributing to the enhanced light trapping capability and the driving force of the Schottky junction at the ZnO/Au interface. The visible spectral photoresponse of ZnO-Au hybrid films mainly results from the hot electron generation and injection process over the Schottky junctions mediated by Au surface plasmons. We believe that the direct nanoimprinting process and hybrid semiconductor/metal system with large scale integration capability and tunable properties presented in this work have an important impact on a variety of optoelectronic devices, such as photodetectors, solar cells and light emitting devices.

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Notes and references

- 1 M. W. Knight, H. Sobhani, P. Nordlander and N. J. Halas, *Science*, 2011, **332**, 702–704.
- 2 H. Qiao, J. Yuan, Z. Xu, C. Chen, S. Lin, Y. Wang, J. Song, Y. Liu, Q. Khan, H. Y. Hoh, C.-X. Pan, S. Li and Q. Bao, ACS Nano, 2015, 9, 1886–1894.
- 3 Z. Wang, M. Safdar, C. Jiang and J. He, *Nano Lett.*, 2012, 12, 4715–4721.
- 4 Z. Lou, L. Li and G. Shen, *Adv. Electron. Mater.*, 2015, 1, 1500054.
- 5 D. D. Li, H. Jun, R. Q. Wu and J. G. Lu, *Nanotechnology*, 2010, **21**, 485502.

- 6 C. L. Hsu and S. J. Chang, Small, 2014, 10, 4562-4585.
- 7 J. Hu, D. Li, J. G. Lu and R. Wu, *J. Phys. Chem. C*, 2010, **114**, 17120–17126.
- 8 D. D. Li, L. Zhao, R. Q. Wu and J. G. Lu, *Nano Res.*, 2011, 4, 1110–1116.
- 9 R. S. Thompson, D. Li, C. M. Witte and J. G. Lu, *Nano Lett.*, 2009, **9**, 3991–3995.
- 10 C. Y. Yan, Z. Tao and P. S. Lee, *Appl. Phys. A: Mater. Sci. Process.*, 2009, **94**, 763–766.
- 11 F. Kim, S. Kwan, J. Akana and P. Yang, *J. Am. Chem. Soc.*, 2001, **123**, 4360–4361.
- 12 K. D. Barbee, A. P. Hsiao, M. J. Heller and X. Huang, *Lab Chip*, 2009, **9**, 3268–3274.
- 13 G. Chen, Z. Liu, B. Liang, G. Yu, Z. Xie, H. Huang, B. Liu, X. Wang, D. Chen, M. Q. Zhu and G. Shen, *Adv. Funct. Mater.*, 2013, 23, 2681–2690.
- 14 K. H. Tsui, Q. Lin, H. Chou, Q. Zhang, H. Fu, P. Qi and Z. Fan, Adv. Mater., 2014, 26, 2805–2811.
- 15 J. E. Yoo, K. Lee, M. Altomare, E. Selli and P. Schmuki, Angew. Chem., Int. Ed., 2013, 52, 7514–7517.
- 16 S. F. Leung, M. Yu, Q. Lin, K. Kwon, K.-L. Ching, L. Gu, K. Yu and Z. Fan, *Nano Lett.*, 2012, **12**, 3682–3689.
- 17 S. F. Leung, Q. Zhang, F. Xiu, D. Yu, J. C. Ho, D. Li and Z. Fan, *J. Phys. Chem. Lett.*, 2014, 5, 1479–1495.
- 18 N. J. Halas, Nano Lett., 2010, 10, 3816-3822.
- 19 Z. Liang, J. Sun, Y. Jiang, L. Jiang and X. Chen, *Plasmonics*, 2014, **9**, 859–866.
- 20 M. W. Knight, Y. Wang, A. S. Urban, A. Sobhani, B. Y. Zheng, P. Nordlander and N. J. Halas, *Nano Lett.*, 2013, **13**, 1687–1692.
- 21 A. Pescaglini, A. Martin, D. Cammi, G. Juska, C. Ronning,
 E. Pelucchi and D. Iacopino, *Nano Lett.*, 2014, 14, 6202–6209.
- I. Park, S. H. Ko, H. Pan, C. P. Grigoropoulos, A. P. Pisano,
 J. M. J. Frechet, E.-S. Lee and J.-H. Jeong, *Adv. Mater.*, 2008,
 20, 489.
- Zi T. Sun, Z. Xu, W. Zhao, X. Wu, S. Liu, Z. Zhang, S. Wang,
 W. Liu, S. Liu and J. Peng, *Appl. Surf. Sci.*, 2013, 276, 363–368.
- 24 Y. S. Oh, K. H. Lee, H. Kim, D. Y. Jeon, S. H. Ko, C. P. Grigoropoulos and H. J. Sung, *J. Phys. Chem. C*, 2012, 116, 11728–11733.
- 25 E. Palik, *Handbook of Optical Constants of Solids Vol I*, Academic Press, Orlando, 1985, pp. 577–580.
- 26 M. Mahanti and D. Basak, Chem. Phys. Lett., 2014, 612, 101-105.
- 27 C. Y. Chen, J. R. D. Retamal, I. W. Wu, D. H. Lien, M. W. Chen, Y. Ding, Y. L. Chueh, C. I. Wu and J. H. He, *ACS Nano*, 2012, 6, 9366–9372.
- 28 U. Ozgur, D. Hofstetter and H. Morkoc, *Proc. IEEE*, 2010, 98, 1255–1268.
- 29 X. Liu, L. Gu, Q. Zhang, J. Wu, Y. Long and Z. Fan, *Nat. Commun.*, 2014, 5, 4007.
- X. Tian, W. Wang, Y. Hao, Y. Lin, Y. Cui, Y. Zhang, H. Wang,
 B. Wei and B. Xu, *J. Mod. Opt.*, 2014, 61, 1714–1722.
- 31 H. Ding, J. Shao, Y. Ding, W. Liu, H. Tian and X. Li, ACS Appl. Mater. Interfaces, 2015, 7, 12713–12718.

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- 32 A. Abou Chaaya, M. Bechelany, S. Balme and P. Miele, *J. Mater. Chem. A*, 2014, 2, 20650–20658.
- 33 M. Lindgren, M. Currie, C. Williams, T. Y. Hsiang, P. M. Fauchet, R. Sobolewski, S. H. Moffat, R. A. Hughes, J. S. Preston and F. A. Hegmann, *Appl. Phys. Lett.*, 1999, 74, 853–855.
- 34 A. M. Soleimanpour, Y. Hou and A. H. Jayatissa, *Appl. Surf. Sci.*, 2011, 257, 5398–5402.
- 35 K. Moazzami, T. E. Murphy, J. D. Phillips, M. C. K. Cheung and A. N. Cartwright, *Semicond. Sci. Technol.*, 2006, **21**, 717–723.
- 36 J. G. Endriz and W. E. Spicer, Phys. Rev. Lett., 1970, 24, 64.
- 37 R. Viter, Z. Balevicius, A. Abou Chaaya, I. Baleviciute, S. Tumenas, L. Mikoliunaite, A. Ramanavicius, Z. Gertnere, A. Zalesska, V. Vataman, V. Smyntyna, D. Erts, P. Miele and M. Bechelany, *J. Mater. Chem. C*, 2015, 3, 6815–6821.