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Wafer-scale self-organized InP nanopillars with controlled orientation for photovoltaic devices

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Abstract
A unique wafer-scale self-organization process for generation of InP nanopillars is demonstrated, which is based on maskless ion-beam etching (IBE) of InP developed to obtain the nanopillars, where the height, shape, and orientation of the nanopillars can be varied by controlling the processing parameters. The fabricated InP nanopillars exhibit broadband suppression of the reflectance, ‘black InP,’ a property useful for solar cells. The realization of a conformal p–n junction for carrier collection, in the fabricated solar cells, is achieved by a metalorganic vapor phase epitaxy (MOVPE) overgrowth step on the fabricated pillars. The conformal overgrowth retains the broadband anti-reflection property of the InP nanopillars, indicating the feasibility of this technology for solar cells. Surface passivation of the formed InP nanopillars using sulfur-oleylamine solution resulted in improved solar-cell characteristics. An open-circuit voltage of 0.71 V and an increase of 0.13 V compared to the unpassivated device were achieved.

Keywords: nanopillar, photovoltaics, ion beam etching, surface passivation, reflection, III-V semiconductors, InP

(Some figures may appear in colour only in the online journal)
radiative carrier recombination. Therefore, it is important to employ materials with low surface recombination velocities and develop efficient surface passivation methods. Both growth and top-down approaches have been used for fabrication of NWs/NPs. In the last few years, much effort has been made to grow III-V NWs for realization of NW solar cells [17]. However, improvement in structural morphology with precise control over their composition, crystal structure, and dopant concentration is still required [18, 19]. In this regard, realizing NW solar cells with radial junctions is advantageous, where relatively lower carrier diffusion lengths in NWs can be compensated for without affecting the cell performance. One of the prominent materials for solar cells is InP, where its direct bandgap offers the advantage of efficient light absorption in very thin layers. Moreover, InP has very high electron mobility and its bandgap (1.34 eV) has very good overlap with the maximum intensity of the solar spectrum. InP also has a low surface recombination velocity (∼10^3 cm s⁻¹), making it a suitable material to realize efficient NP solar cells [6, 17, 20, 21]. For large-scale fabrication, cost effectiveness is an important issue [6, 16, 20, 22]. Top-down approaches are particularly interesting for fabrication of NP solar cells with conformal p–n junction geometry, where there is no need to electrically insulate the NPs by embedding them in another layer. Using the NP geometry, it is also possible to move toward flexible solar cells by embedding the NPs in a flexible matrix. For example, an epitaxial ‘lift-off’ process in which the thin-film layer is separated from the substrate using an InGaAs sacrificial layer, can enable the reuse of the original InP substrate and thus minimize the total cost [3, 21, 23, 24].

Here we report a unique and low-cost method to fabricate InP NPs with high optical quality at wafer scale without any requirement for patterning. The InP NPs show a broadband suppression of reflectance. As a proof of principle, we demonstrate InP NPs solar cells fabricated by the presented method. For this purpose, a conformal p–n junction for carrier collection is achieved by a metalorganic vapor phase epitaxy (MOVPE) overgrowth step on the fabricated pillars. Consequently, a sulfur-oleylamine-based passivation method was used to improve the performance of the solar cells by increasing the open-circuit voltage.

2. Experimental method

The InP NPs were fabricated using an ion-beam etching (IBE) tool. IBE is a general term used to denote etching techniques that use a collimated ion beam. The ion-beam sputtering-induced formation mechanism of InP NPs is discussed in section 3. Here, we use a directional ion beam of nitrogen ions, which physically etches the material. We used an Ionfab300Plus ion-beam etching system from Oxford Instruments to fabricate the InP NPs. Prior to etching, the InP samples were cleaned with acetone and isopropanol, followed by rinsing with deionized water and then blown dry using nitrogen. Before ion sputtering, the samples were pre-heated at 230 °C for 20 min. The sample temperature is a crucial parameter in the formation of indium-rich clusters during ion bombardment on the surface. However, we note that the actual sample temperature during sputtering could be higher due to contribution from ion bombardment. The etching was carried out at the following optimized processing conditions: Platen rotation speed of 20 rpm and chiller for platen cooling was set on 15 °C. 13 sccm flow of nitrogen with the beam current of 100 mA corresponding to 0.6 mA cm⁻² was used for etching. The ion energy was in ~400 eV and the helium backside cooling at 15 Torr was used. Details of the fabrication steps of the InP NP solar cells, including epitaxial overgrowth of InP on the fabricated InP NPs by MOVPE, surface passivation of InP NPs, and electrical/optical characterization methods can be found in the Supporting Information.

3. Results and discussion

The formation of the InP NPs occurs via a maskless and self-organized process, utilizing ion-beam etching of InP. Previous reports on formation of nanostructures by ion-beam etching have used heavier ions with higher ion energies [25, 26] and therefore the optical properties of the structured materials have been greatly degraded. Here we develop a process using nitrogen ions with energies of only a few hundred eV instead of the commonly used ion energies in the keV range. Here, for the first time to our knowledge, we deploy self-organized InP nanostructures fabricated by ion-beam etching and demonstrate an InP NP solar cell.

The formation of NPs on InP is due to the preferential sputtering of phosphorous, leading to indium enrichment at the surface. The excess indium diffuses on the surface and forms clusters that act as local masks leading to the formation of the InP NPs. The diffusion/migration of these excess atoms increases with temperature. Additionally, the continuous ion bombardment provides extra energy to the migrating atoms, which is usually modeled as lowering the energy barrier for diffusion. The migrating indium atoms gather around nucleation sites available within the diffusion length. Newly liberated indium atoms preferentially join the already existing clusters. Thus, during ion bombardment, indium-rich cluster formation occurs as the surface topography evolves, which generates the NPs and at the same time the energetic ions also sputter the formed clusters. Eventually, when the NP height becomes longer than the diffusion length of the excess indium atom, sputtering of the clusters dominates their growth. The dynamics of surface evolution during ion bombardment/sputtering of InP is complex since it involves modification of surface morphology, chemical composition, and thermally/ ion-assisted enhanced surface diffusion of atoms. Thus, several parameters affect the InP NPs formation, e.g., the sample temperature, ion species, ion-beam energy, density, angle of incidence, and initial conditions such as pre-heating. A detailed understanding of the mechanisms of formation of InP NPs by ion bombardment, including achievable NP size and shape, spatial density, material quality, and elemental distribution requires extensive study, investigating the influence
Figure 1. Fabrication of self-organized InP nanopillars using ion-beam etching. (a)–(d) SEM images of InP nanopillars for different etching times. Scale bars represent 200 nm. (d) 40° orientation angle between the ion beams and the normal direction to the sample surface results in tilted nanopillars. (e) Schematic illustration of the InP nanopillar formation process. The arrows indicate the sputtering nitrogen ions. The indium-rich cluster at the top serves as a mask for further etching. The surface of the pillar is amorphous InP. The indium-rich regions at the top and the amorphous parts at the surface can be removed by hydrofluoric (HF) acid.

Figure 2. (a) TEM image of a single InP nanopillar. The area within the white dashed lines indicates the crystalline InP, which can be seen in (b) after HF treatment of the sample. Representative EDX spectrums for different locations on the pillar are also presented. The top segment of the nanopillars shows a very strong indium peak, indicating the material in this region is In-rich. (b) TEM image of a single InP nanopillars after HF treatment. (c), (d) High-resolution TEM images of the InP nanopillar after HF treatment.
From our preliminary investigations, we find that the NPs spatial density and height can be changed within a certain range by modifying process parameters. By increasing the sputtering time from 30 s to 10 min, the NP height could be changed from about 100 nm to ∼0.8 μm. Further sputtering resulted in needle-like NPs, saturating at a height of about 2–2.5 μm and the etch-front propagated without appreciable change in the topography. However, due to prolonged sputtering it is more likely that these NPs have significant ion-induced damage. Platen temperature plays an important role and NP-like structures (as in figure 1) were observed around 200 °C. Below this temperature, although indium enrichment occurs on the surface no clear NP formation was obtained. With ion energy of 400 eV and platen temperature of 230 °C, InP NPs with ∼200 nm average spatial distances were obtained. We believe it is possible to vary the average spatial separation of the NPs by optimizing the ion energy, ion density, and sample temperature to balance the indium-diffusion, formation, and sputtering of the indium-rich clusters.

Figure 1(a) shows the scanning electron microscope (SEM) image of an InP sample after 30 s etching; the platen temperature was 230 °C. At this stage, we can only see the indium clusters formed on the sample surface in the initial phase of pillar formation.

Figures 1(b) and (c) show representative scanning electron microscope (SEM) images of InP NPs after 5 and 10 min of sputtering, respectively. Thus, the NP height increases with sputtering duration. As shown in figure 1(d), it is also possible to fabricate NPs with tilted orientations by controlling the sample tilt with respect to the incident ion beam. Figure 1(e) shows a schematic illustration of InP NP formation. The excess indium formation at the top serves as the etch mask. During ion sputtering, diffusion of indium atoms to the top of the NPs continues to occur, and the side walls are composed of amorphous P-rich InP formed by redeposition. In fact, the redeposited layer is advantageous as it protects the crystalline part of the pillars from damage from the etching ions. This mechanism leads to formation of pure crystalline InP only at the core of the NPs. The surface amorphous layer as well as the indium-rich pillar top can be wet-chemically removed, using HF etching.

The formation of InP NPs occurs from the surface due to independent control of the sample temperature. This is also
feasibility of employing the fabricated InP NPs in solar-cell devices. For this purpose, we used epitaxially grown InP samples, which consisted of 1 μm thick p-type \( (10^{17} \text{ cm}^{-3}) \) InP layer on a p+ InP substrate \( (10^{18} \text{ cm}^{-3}) \). Subsequently, NPs with the optimized geometry (800–900 nm of height, 200 nm average spatial distance, 150 nm/200 nm of top/ bottom width), which demonstrate very low total reflectance (supporting information, figure S1), were fabricated on this wafer. As mentioned previously, NP geometry can be very useful in suppressing the reflectance over a broad spectral range and consequently increasing the light absorption, which is a very important property for solar cells. The disordered nature of the self-organized NPs, obtained in this case, can potentially be advantageous for enhanced light absorption compared to a periodic geometry [27, 28].

The formation of a conformal p-n junction is an important step in realizing a solar-cell device. This not only provides a large carrier collection (p-n junction) area, but also retains the anti-reflection property of the etched NPs. There are different approaches to forming p-n junctions in such structures, such as ion implantation [29] or surface doping [20]. Here we used epitaxial InP overgrowth of the self-organized InP NPs arrays with n+ doping, \( \sim 2 \times 10^{19} \text{ cm}^{-3} \), and 30 nm thickness to realize a nearly conformal p-n junction. The overgrowth step was optimized for controlled lateral growth and doping levels. Figures 3(a)–(c) show representative SEM images of the NP samples at different process steps in the fabrication of conformally overgrown InP NPs. Importantly, as shown in figure 3(d), the anti-reflective property of the NPs is not degraded after overgrowth, supporting the fact that the overgrowth is conformal. After overgrowth, the back ohmic p-contact was made by evaporating Au/Zn/Au (10/30/200 nm). The front n-contact was made by depositing a transparent conductive aluminum doped zinc oxide (AZO) layer on the overgrown surface using atomic layer deposition (ALD). Here we note that the deposited AZO layer thickness \( \sim 120 \text{ nm} \) was not optimized in terms of optical performance of the NP structure. Thus, although the AZO deposition is conformal, the non-optimized layer thickness affects the optical performance (suppression of reflectance).

Figure 4 shows a schematic sketch of the envisioned NP solar cell with a conformal p-n junction and a conformal AZO contact layer. Subsequently, silver finger contacts were formed on the AZO layer. The \( I-V \) characteristics of the fabricated NP solar cell are shown in figure 5(a). The light \( I-V \) responses of the solar cells were measured under 100 mW cm\(^{-2}\) of solar simulated AM1.5G illumination. Considering the relatively short NPs \( \sim 800 \text{ nm} \), it is unlikely that all light (above the InP bandgap) is absorbed in the NPs. We believe that in our device we have contribution from both absorption in the InP NPs as well as from the region below. To determine if the contribution from the NPs dominates, a detailed spectral analysis including full electromagnetic simulations to understand the behavior of light (localization, waveguiding, scattering, and absorption) in the self-organized NP samples is required.

![Figure 5](image)

Figure 5. (a) \( I-V \) characteristics under dark and AM 1.5G illumination for the fabricated InP nanopillar solar cells. The inset shows an image of the fabricated cell. (b) \( I-V \) characteristics under 1-sun illumination after and before sulfur passivation of InP nanopillars. The open-circuit voltage improves about 0.13 V. The passivation effect can also be observed by the higher photoluminescence intensity (supporting information, figure S2).

attractive because an ion-sputter tool is relatively simpler, as it does not involve the use of corrosive/toxic etch chemistries. In principle, the method can be applied to other III-V materials, binaries, and alloys where the sputter yields of the group III and V species differ. As explained earlier, the mechanism for the formation of InP NPs starts with the highly enriched indium cluster. Indeed, transmission electron microscopy (TEM) images from single InP NPs reveal this and energy dispersive x-ray (EDX) analysis confirms the material content in each segment of NPs (figure 2(a)). For any device structure, it is important to remove the amorphous layers (on the top and sides) with HF. Figure 2(b) shows the TEM image of a single InP NP after HF treatment. As can be seen from the high-resolution TEM images (figures 2(c) and (d)), the crystalline quality of the material is evident.

In the following, we discuss the application of the InP NPs for solar cells. We demonstrate, as a proof of concept, the
Surface states are a major concern for most III-V semiconductor devices [30–32]. Additionally, the process steps in NP fabrication can also introduce surface defects. The existence of carrier traps on the surfaces would be a limiting factor for device performance, since they are a major source of carrier loss. Non-radiative recombination hinders the carrier density buildup, which limits the open-circuit voltage [33]. Hence, an effective passivation method to reduce the surface recombination rate by passivating the surface states is critical. To address this issue, here we used a passivation method based on organic polysulfide by dissolving sulfur in oleylamine [34, 35]. Details of the passivation procedure can be found in the supporting information. The passivation effect was qualified by photoluminescence spectroscopy by comparing the PL-yield (intensity) before and after passivation, which is about two times (supporting information, figure S2) higher after passivation. Figure 5(b) shows a comparison between the passivated and unpassivated NP solar cell. A dramatic increase in the open-circuit voltage (0.13 V) is an indication of the effect of surface passivation for the fabricated NP solar cell. The enhancement in open-circuit voltage results in improvement of the total efficiency from 4.1% to 5.3%. The low-current density level can be attributed largely to the effect of the non-optimized AZO layer on the NPs. In fact, InP NPs show higher reflectance after deposition of AZO, with an increase of 2% to 10% in total reflectance (supporting information, figure S4). By optimizing the AZO deposition, the extracted current is expected to be higher.

4. Conclusion

In conclusion, we demonstrated a novel wafer-scale lithography-free method based on nitrogen ion-beam sputtering to fabricate InP NPs with high optical quality. The height and shape of the NPs could be varied by tuning the etch parameters. The orientation of the InP NPs can be modified from vertical to tilted configurations. In principle, the presented fabrication method can be applied to other III–V materials, binaries, and alloys where the sputter yields of the group III and V species differ. The fabricated InP NPs show a broadband suppression of reflectance, which is very interesting for solar-cell applications. As a proof of principle, we fabricated solar cells using self-organized InP NPs with a conformal p-n junction. We used a sulfur-based solution for surface passivation, and solar cells fabricated from passivated NPs show an open-circuit voltage of 0.71 V, an increase of 130 mV compared to the untreated sample. This increase results in improvement of the total efficiency from 4.1% to 5.3%. Using optimized cell design (doping, layer thickness, etc) and the electrical contacts, the performance of the cell can be improved. The presented passivation method can also be applied to other III–V solar cell materials. This can be particularly interesting for GaAs-based solar cells, where effective passivation of surface states is required.

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