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Solution Process of Large Scale High Sensitivity ZnO/Si Hierarchical Nano-heterostructure Photodetectors

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TEM study of ZnO/Si Branched NW Interface:

Cross-sectional transmission electron microscopy (XTEM) is used to study the interface between ZnO nanowire branches and Si nanowire cores (figure s1).

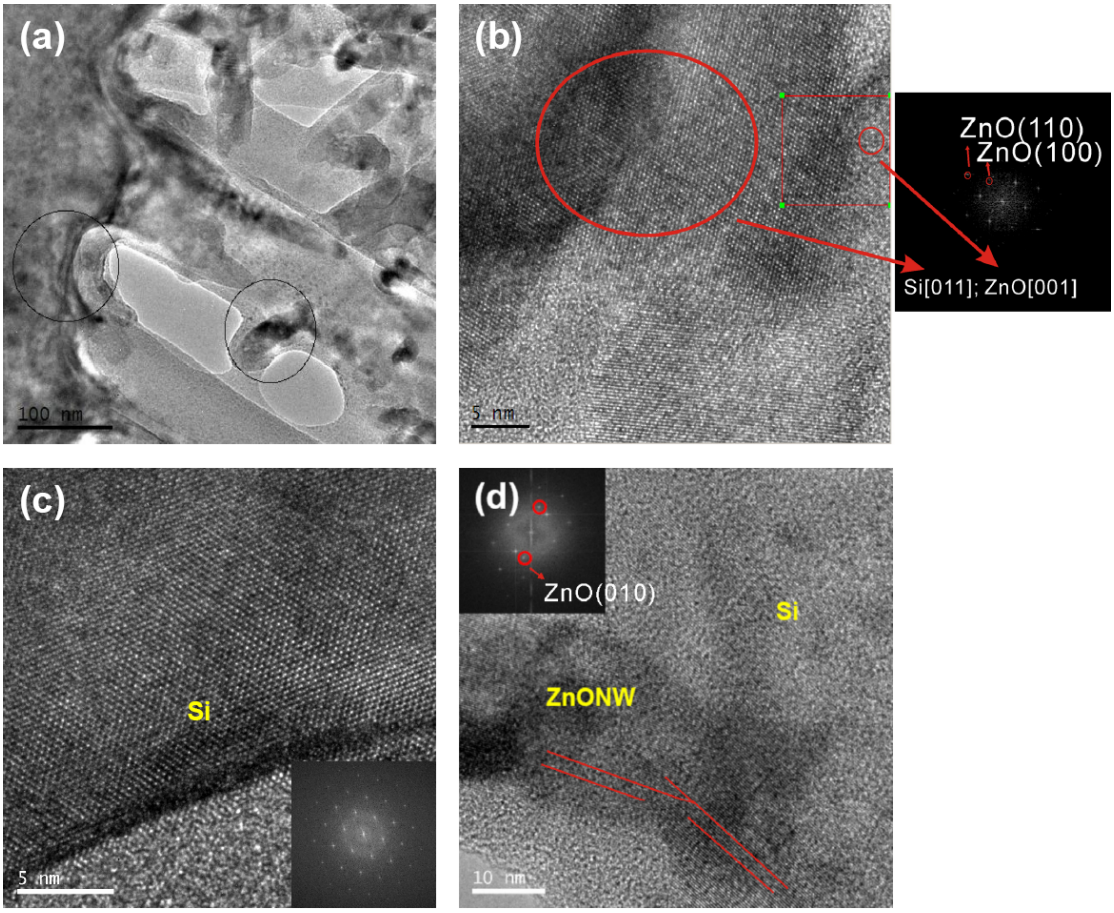

Figure s1. Cross-sectional TEM image on branched ZnO/Si heterostructure (a), a zoom-in view on one Si nanowire surface with ZnO nanoparticles from sputtering seeding process (b), a zoom-in view on the bottom of the etched Si substrate (c), and a zoom-in view on the interface between a ZnO and Si nanowire (d).

Figure s1-a shows a chemically etched Si substrate with ZnO NW branches. Different positions are investigated. Distribution of ZnO nanoparticles with diameter in the range of 10-20 nm is observed over the surface of Si nanowires limited by the Si nanowire geometry.

Figure 1s-b shows a representative high resolution TEM image of ZnO crystalline nanoparticles from the seeding process, found near the lower part of Si nanowires. As shown in the image, two

particles are showing difference in size and orientation. It can be concluded that a random heteroepitaxial growth of nanoparticles on the Si nanowire surface is due to the roughness of Si nanowire surface from the chemical etching. Nevertheless, no amorphous silicon oxide is found between ZnO nanoparticles and Si nanowires, owing to the efficient oxide etching prior to sputtering seeding layer.

Figure 1s-c shows a clean interface at the bottom of the chemical etched Si nanowire array.

Figure 1s-d shows one single ZnO nanowire growing on Si nanowire along 002 c-direction with a lattice spacing 2.62 Å. Again, a clean interface is observed with absence of an amorphous silicon oxide layer. Removing the oxide layer is important to form epitaxial growth of ZnO nanowire branches on Si nanowire core.[1] It is reported in previous studies that failed coating of ZnO seeding on Si nanowire surface after removing native oxide is observed. However, TEM studies reveal that in our work low pressure sputtering is effective to deposition ZnO nanoparticles into high aspect ratio SiNW array and onto the surface of SiNW surfaces. HRTEM reveals that the ZnO nanowire is not growing perpendicular to the Si nanowire surface, but with a small angle (Figure s-1d).

As seen above, HF is removed effectively before seeding process. A fairly high dark current and low J_P and J_D ratio is observed (the highest J_P/J_D we got is 250 at reverse bias -1 V). On the other hand, on-going research is also focused on study the oxide effect on the device photoresponse performances. Because it is believed that effective passivation from oxide layer to the surface defects on Si nanowire surface can reduce the recombination rate at the interface and thus the J_P/J_D ratio. This study is not included in this work.

Material growth and device fabrication procedure:

P-type boron doped silicon (111) with thickness of 250 µm (1-10 ohm.cm, waferworld) wafers were cleaned with solvent, rinsed with deionized water and dried with N_2. Si wafer was then fixed on a homemade etching with water bath at 50 °C and emerged in a mixture solution of $AgNO_3$ and HF solution. After etching for certain amount of time, sample was taken out and rinsed with DI water. Then etched sample was placed in 1:10 diluted nitric acid cleaning solution for 2 hrs to remove Ag deposition formed during the chemical etching. ZnO seeding layer was then deposited on the SiNW substrate with low pressure RF sputtering using 99.99% ZnO target. Prior to seeding, SiNW samples were dipped in buffered oxide etching (1:6 BOE) solution for 10 s to remove native oxide. Then samples were spary-cleaned using DI water, dried with N_2, and immediately transferred to deposition chamber. During the Argon plasma sputtering, pressure in the chamber was maintained at 1.7 mtorr. The deposition rate was first characterized on planar silicon substrate. A thin layer of ZnO with 45 nm in thickness was then achieved after 16 mins. Same recipe was used for seeding SiNW samples. Hydrothermal growth of ZnO nanowires was reported before [2]. Briefly, 25 mM solutions of zinc acetate and HMTA (Sigma) in DI water (>17.6 MΩ cm) were prepared. Substrates were fixed on a supporting glass slides with top side down and immersed in the reaction solution. The reactor was placed in an oil bath and the inner temperature was maintained at 85°C with gentle agitation at 200 RPM for 3.5 hrs. The as-growth samples were ultrasonicated at low power (<30 W), then thoroughly rinsed with DI water, and blow dried with N_2. Samples are stored under low pressure and N_2 environment. ZnO/Si branched heterostructure arrays were embedded in poly(methylglutarimide) (PMGI SF-6, Microchem). Plasma dry etching was applied to the sample surface to remove polymers and

expose ZnO tips for top contact. 200 nm thick ITO was deposited as the transparent top contact (resistivity 3×10^{-3} Ω·cm and transmittance higher than 50%). Titanium and gold were then deposited on the corner of the ITO. Indium was applied at the back of boron-doped Si for back contact for ohmic contact.

Single SiNW characterization:

Si NWs were ultra-sonicated from substrate and suspended in IPA solution, then dropped on silicon substrate with thermally grown oxide (600nm). Al/Au was patterned as source-drain contact by the e-beam lithography. Devices were tested, from which the Si NWs with diameter of 60nm showed carrier concentration 10^{15} cm^{-3}, and mobility 3.2×10^{-2} $cm^2/V\cdot s$.

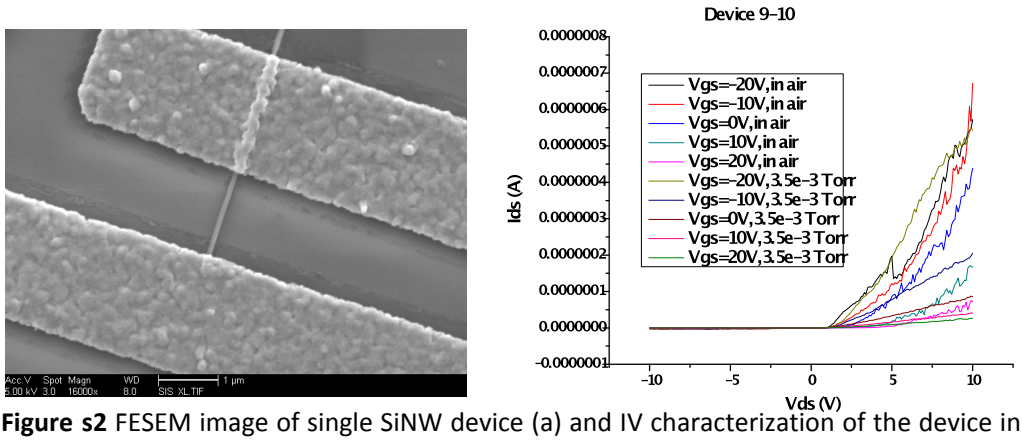

Figure s2 FESEM image of single SiNW device (a) and IV characterization of the device in air and vacuum at room temperature.

Current-Voltage (I-V) characterization:

Boron doped p-type Si with a resistivity of 1-10 ohm-cm has a doping level of 10^{15}–10^{16} cm^{-3}. Contact on boron doped p-type Si using low working function metal such as aluminum[3], indium[4-6] or Indium alloy[7] as back ohmic contact is reported in literature. Indium paste with a fairly large area is soldered at the back of a p-type Si piece and tested. Contact properties of Ti/Au/ITO layer on n-type ZnO are studied in details by Kang et al[8]. IV characterization of contacts are measured and shown in figure s3.

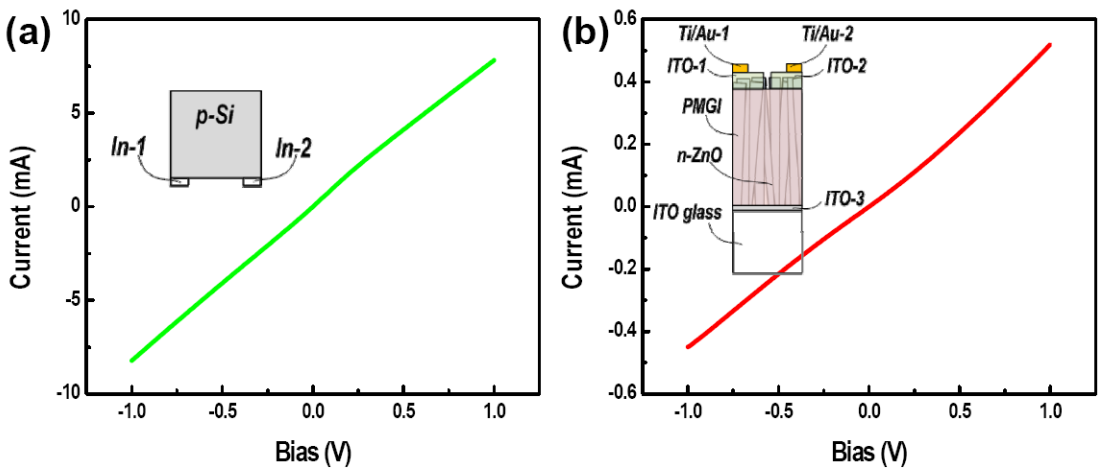

Figure s3 Current-voltage (IV) characterization of contact properties: a) Indium on plain p-Si and b) Au/Ti/ITO on ZnO nanowire array.

Photoresponsivity measurement:

Room temperature photoresponse was conducted using monochromator (Horiba Jobin Yvon iHR 550) equipped with a 100 W halogen lamp (Osram 64628) and a 1200 groove/mm grating with 330 nm blaze. Illumination was incident at 45° to the sample surface. Keithley 2410 source meter was used.

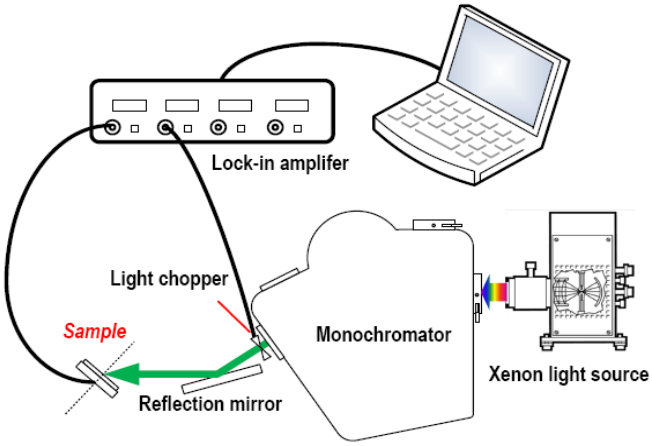

Figure s4 Photoresponse measurement setup

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