Photoinduced modification of surface states in nanoporous InP

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Porous honeycombs of n-type InP were investigated by terahertz time-domain and x-ray photoemission spectroscopies. After photoexcitation the dark conductivity was found to increase quasi-irreversibly, recovering only after several hours in air. The calculated electron density for different surface pinning energies suggests that photoexcitation may reduce the density of surface states. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3697410]

A precise control of the surface properties of semiconductor nanomaterials is vital for their functionality and use in many opto-electronic applications. Porous semiconductors[1] have been investigated as birefringent[2] and non-linear optical media[3,4] and as emitters of terahertz radiation.[4,5] Giant surface areas and high aspect ratios makes them attractive as functionalized surfaces in biochemical sensors.[6,7] Terahertz time-domain spectroscopy allows the non-contact investigation of electron transport in semiconductor nanomaterials[8] and has been used to determine the equilibrium and photoconductivity of porous InP.[9,10] The technique allows the photoconductivity to be determined on picosecond timescales, provided that the material's properties are not permanently altered by photoexcitation.

In this article, we report that the photoexcitation of nanoporous InP honeycombs quasi-permanently increases the conductivity of the material, with the conductivity remaining high over 1 h after the photoexcitation beam is blocked. Terahertz time-domain spectroscopy was used to measure the transmission of InP porous membranes with varying donor density and orientation. Calculations and x-ray photoemission spectroscopy (XPS) were utilized to examine the charge density and composition of surface states.

Porous InP honeycombs were produced by the electrochemical etching[1,11] of ⟨100⟩ and ⟨111⟩ oriented n-type InP (with a donor density of either $N_1 = 1 \times 10^{17}$ cm^{-3} or $N_2 = 9 \times 10^{18}$ cm^{-3}), producing curropores perpendicular to the samples' surfaces. In Fig. 1(a), typical scanning electron micrographs are shown for curropores running normal to the surface of the low doping (left) and high doping (right) substrates. While the areal fill fraction f is comparable for the two samples, the width of the InP walls is 125 ± 5 nm for the low doping case and 48 ± 7 nm for the high doping case. Cross-sectional electron microscopy images verified that the pores had uniform diameter and extended throughout the sample's thickness ($d = 32\,\mu$m for high doping and $d = 50\,\mu$m low doping).

In order to investigate dc current flow over macroscopic in-plane distances, current-voltage characteristics were obtained from electrically contacted devices. Initially the current at low voltages is a few nA, as the solid line in Fig. 1(b) illustrates for ⟨111⟩-oriented, $N_d = 9 \times 10^{18}$ cm^{-3} pores in a sweep from 0 V to 10 V taking 1 s. This is many orders of magnitude below the current for a bulk reference sample with the same doping (data not shown), which was 75 mA at 0.1 V. Macroscopic transport is hindered in porous InP by the proximity of the surface, which depletes the material of electrons (see below). At higher voltages, the current flow in the porous samples is unstable, and a step increase is witnessed at 5 V. The second current-voltage characteristic (dashed line) exhibits a higher current at low voltages. Repeated sweeps (not shown) have shapes similar to the second sweep, while if the samples are left in air for a couple of minutes without bias then the initial characteristic is obtained upon repeating the experiment. This behaviour suggests that the injection of energetic electrons alters the conductivity of

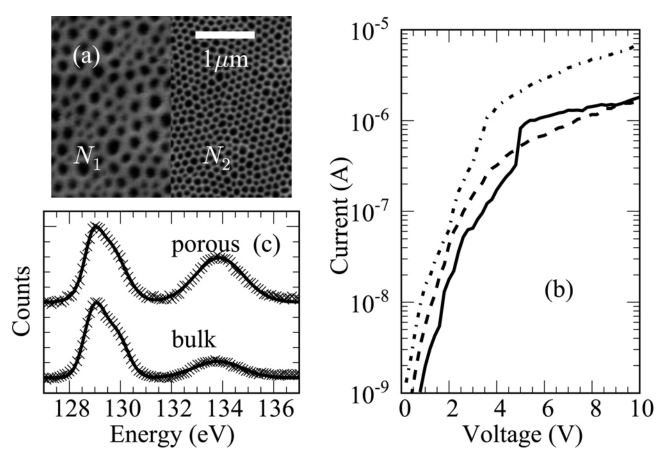

FIG. 1. (a) Electron micrograph of the surface of (100)-oriented curropores in n-type InP doped at $N_1 = 1 \times 10^{17}$ cm^{-3} (left) or $N_2 = 9 \times 10^{18}$ cm^{-3} (right). (b) Current-voltage characteristics in the dark (initial sweep, solid line; second sweep, dashed line) and under illumination at 800 nm (dashed-dotted line). (c) XPS spectra of the phosphorous 2p core-levels of (100)-oriented bulk and porous InP.

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