Pore Etching in III-V and II-VI Semiconductor Compounds in Neutral Electrolyte

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We propose to use a neutral electrolyte based on an aqueous solution of NaCl instead of commonly used aggressive acids or alkaline electrolytes for the purpose of electrochemical nanostructuring of GaAs and CdSe substrates. It is shown that the process of material porosification can be controlled by the conditions of anodic etching. A photoluminescence analysis of the porous structures obtained and referenced to the as-grown substrate demonstrates that an effective passivation of the surface occurs during anodization in this electrolyte. The results obtained pave the way for the development of optoelectronic devices based on electrochemically nanostructured GaAs and CdSe compounds, particularly for high-efficiency solar cells.
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Over the last decades, it was demonstrated that material properties can be engineered by nanostructuring, i.e., by tailoring the architecture of macroscopic structures on the nanometer scale. Electrochemistry is one of the most accessible and cost-effective approaches for tailoring the architecture of semiconductor materials on the submicrometer scale by introducing porosity.[1,2] A variety of porous semiconductor architectures have been demonstrated, including self-organized periodic spatial distribution of pores achieved by anodic etching.[3] Because of the nanoscale nature of light absorption and photocurrent generation in solar energy conversion, the advent of methods for controlling inorganic materials on the nanometer scale opens new opportunities for the development of future generations of solar cells.[4] GaAs is one of the most suitable materials for these purposes because its bandgap fits the maximum of the solar energy distribution well. Recently, the applicability of a porous GaAs electrode in a photoelectrochemical solar cell was demonstrated.[5] It was shown that the introduction of porosity in the GaAs photoelectrode leads to a considerable photosensitivity increase in the long wavelength region near the bandgap, which results in an increase of the output power by a factor of four in comparison to a cell based on a bulk GaAs electrode. Apart from GaAs, some II-VI compounds, including CdTe and CdSe, are promising materials for efficient solar cells. To promote the development of photoelectrochemical cells based on porous semiconductors, the method of generating porosity should include conditions for effective surface passivation.

The pores in semiconductors are usually introduced via electrochemical dissolution of materials in electrolytes containing acids such as hydrofluoric acid (HF), HCl, H_2SO_4, HNO_3, etc., or alternatively in alkaline electrolytes. To make the process of nanofabrication based on anodic etching broadly accessible and environmentally friendly, we demonstrate in this article the possibility of pore formation in GaAs and CdSe using aqueous solutions of NaCl. The photoluminescence (PL) characterization of the prepared structures indicates an effective passivation of the huge internal surface of the porous structures, making them suitable for application in optoelectronic devices including solar cells.

Crystalline 500 μm thick (111)-oriented substrates of Si-doped n-GaAs with a free electron concentration of 2×10^{18} cm^{-3} and wurtzite-phase crystalline substrates of n-CdSe with a free electron concentration of 1×10^{18} cm^{-3} were used. The anodic etching was carried out at $T = 23°C$ in 3.5 M NaCl aqueous solution in an electrochemical double cell as described elsewhere;[6] the area of the

sample exposed to the electrolyte was 0.25 cm^2. The electrolyte was pumped through both cells in a continuous mode. A Tescan scanning electron microscope (SEM) equipped with an Oxford Instruments INCA energy dispersive X-ray (EDX) system was used to analyze the morphology and chemical composition of the porous samples.

PL was excited by the 514 nm line of an Ar$^+$ SpectraPhysics laser and analyzed through a double spectrometer. The resolution was better than 1 meV. The samples were mounted on the cold station of a LTS-22-C-330 cryogenic system.

Figure 1a presents a cross section (obtained by cleavage) of a typical porous sample produced by anodic etching of a n-GaAs substrate embodying three dissolution-step current densities of 75, 50, and 25 mA/cm^2, respectively, and a duration of 5 min each. The image shows the formation of three porous layers with a thickness of about 40 μm each and a degree of porosity that depends on the anodization current.

As shown earlier,[2] two types of pores can be introduced in III-V semiconductor compounds, namely crystallographically oriented or "crysto" pores and current-line oriented or "curro" pores. Crysto pores are usually generated due to direct dissolution of the material. They grow along ⟨111⟩B directions of the zincblende structure and are bounded by pore walls defined by three available crystallographic {112} planes. Exhibiting a triangular-prism-like shape, the pores involved reflect the anisotropy of anodic etching inherent to semiconductor compounds. Triangular-prism-shaped pores are clearly seen in the top view of the sample inset in Fig. 1a, therefore suggesting the formation of crysto pores. This observation is also supported by the polarization curve presented in Fig. 2a. The anodic current increases steeply when increasing the voltage, which is characteristic for the direct dissolution of the material. The pore-formation potential deduced from the polarization curve is around 4 V.

Figure 1b represents a typical cross section of a porous CdSe sample produced by potentiostatic anodization of a crystalline substrate for 15 min under an applied voltage of 18 V. The cross-sectional view, as well as the top view inset in Fig. 1b, suggests the formation of curro pores. Figure 2b shows the polarization curve measured at the beginning of the anodization process. Starting from low voltages, the reverse current first increases slowly with the applied potential, then increases sharply around 16 V and reaches a maximum around 17 V. The decrease of the current after the peak, followed by a strong increase, may be attributed to oxide formation, making current flow somewhat more difficult before complete breakdown occurs. Because the growth of current-line-oriented pores actually requires the dissolution of the oxide at the pore tips,[2] one may assume that some extreme conditions (e.g., high local elec-