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Selective formation of porous layer on n-type InP by anodic etching combined with scratching

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Abstract

The selective formation of porous layer on n-type InP (0 0 1) surface was investigated by using scratching with a diamond scriber followed by anodic etching in deaerated 0.5 M HCl. Since the InP specimen was highly doped, the anodic etching proceeded in the dark. The potentiodynamic polarization showed the anodic current shoulder in the potential region between 0.8 and 1.3 V (SHE) for the scratched area in addition to the anodic current peak at 1.7 V (SHE) for the intact area. The selective formation of porous layer on the scratched are was brought by the anodic etching at a constant potential between 1.0 and 1.2 V (SHE) for a certain time. The nucleation and growth of etch pits on intact area, however, took place when the time passed the critical value.

The cross section of porous layer on the scratched area perpendicular to the [$\bar{1}$ 1 0] or [1 1 0] scratching direction had a V-shape, while the cross section of porous layer on the scratched area parallel to the [$\bar{1}$ 1 0] or [1 1 0] scratching direction had a band structure with stripes oriented to the [$\bar{1}$ 1 1] or [1 $\bar{1}$ 1] direction. Moreover, nano-scratching at a constant normal force in the micro-Newton range followed by anodic etching showed the possibility for selective formation of porous wire with a nano-meter width.

Keywords: Porous layer; n-type InP; Scratching; Anodic etching; Selective formation

1. Introduction

Since the discovery of visible luminescence from porous silicon formed on silicon by anodic etching in HF solutions [1,2], many studies have been focused on the formation process and mechanism of porous layer as well as its light emission process due to a variety of potential applications for optoelectronics and electronic devices fabrication. Recently, it was found that a porous layer is formed on compound semiconductors such as GaAs [3,4] or InP [5–7] by anodic etching in halogenic acids or sulfuric acid. It was also reported that the morphology of porous layer on InP depends on the type of electrolyte [7]. Visible photoluminescence in the green wavelength region of the spectrum was observed from porous GaAs formed by anodic etching in HCl or Cl^- containing solutions [8]. On the other hand, visible photoluminescence in the yellow to red range of the spectrum was observed from porous layer formed on n-type InP (1 0 0) with high dopant level by anodic etching in the dark in HF [7].

Other recent topics with respect to semiconductors is the formation of metallic nanostructures such as nano-dot array and nano-wires on top of semiconductor substrate due to the increased demand for electrical interconnections in microelectronics, microsensors, and patterned media for magnetic storage. Patterned metal deposition on semiconductor surfaces is usually carried out by using different indirect methods such as photolithography combined with metal evaporation, electro- or electroless-deposition, or molecular beam epitaxy. In addition to indirect patterning techniques, the development of direct patterning methods are now in progress by using a focus ion beam (FIB) bombardment [9–11] or an atomic force microscope (AFM) [11–15]. The introduction of defects on the semiconductor surface due to a FIB bombardment allowed one to realize selective metal electrodeposition in the defective regions. Nano-indentation or nano-scratching

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to the semiconductor surface by using an AFM equipped with a diamond tip also introduced the local defective regions, in which the selective metal electrodeposition took place, and made possible the formation of metal dot array or metal wires. The works of patterned metal deposition by a FIB bombardment or an AFM, however, were mainly directed to silicon substrate surface.

The pattering of semiconductor surfaces with porous layer may be one of interesting subjects with respect to optoelectronics and microelectronics. Schmuki et al. [7,9] have suggested the possibility for selective formation of porous layer on silicon, GaAs or InP by a FIB bombardment or a scratching with a diamond indenter. However, the selective formation of porous layer in the defective regions of semiconductor surface by anodic etching is not well understood because of few studies in this field. The scratching with a diamond indenter may be convenient and not expensive technique for the selective formation of porous layer as compared to the FIB bombardment.

In this study, as the first step, anodic etching of n-type InP in HCl after scratching by a diamond scriber was performed to explore the possibility for local formation of porous layer and to find the optimum condition of anodic etching for the formation of porous layer. Secondly, the formation of the more fine porous wires on InP was tested by combining nano-scratching with anodic etching in HCl.

2. Experimental

The materials used were n-type InP (0 0 1) wafers doped with (3.3–4.7) $\times 10^{18}\,cm^{-3}$ of sulfur. The ohmic contact on the backside of the wafer was made with annealing in nitrogen gas at 330–380 °C after the formation of successive layers (Au–Ge, Ni and Au) by a vacuum evaporation. The InP wafers were cut into a size of 1.2 cm × 1.2 cm along the cleavage plane. Prior to each experiment, the specimens were degreased with ethanol and dried with nitrogen gas. The specimen surfaces were manually scratched to the [1 1 0] and [$\bar{1}$ 1 0] directions in air at a normal force of 2–5 N with a diamond scriber to draw 10 scratched lines with a length of 4 mm which were crossed each other. The tip shape of the diamond scriber was almost conical.

Afterwards, the specimen was set via an O-ring in an electrochemical cell made from Diflon and the surface area of 0.283 cm^2 was exposed to the electrolyte. A platinum net and a silver/silver chloride electrode were used as counter electrode and reference electrode, respectively. All potentials in this paper are referred to a standard hydrogen electrode (SHE). The electrolyte solution was 0.5 M HCl which was prepared from reagent grade chemicals and ultrapure water (Millipore Q). The solution was deaerated with ultrapure argon gas before and during experiments to avoid the possibility of cathodic current flow due to reduction of residual oxygen in the solution during anodic polarization. The specimens were anodically polarized at a constant potential for a certain time in deaerated 0.5 M HCl in dark. A light illumination during anodic etching of n-type InP was not necessary for formation of porous layer since a tunneling breakdown occurred easily due to sufficiently high doping level of the specimens. The surface and cross sectional morphologies of intact and scratched areas after anodic etching were observed with scanning electron microscopy (SEM).

Moreover, a nano-scratching at a constant normal force in the micro-Newton range was tested to the specimen surface to explore the possibility for formation of more fine porous wires by the subsequent anodic etching. The nano-scratching apparatus (Hysitron Co. Ltd., Triboscope) was combined with AFM (Digital Instruments, Nanoscope IIIa). The specimen surface as the first trial was scratched to either the [1 1 0] or [$\bar{1}$ 1 0] direction in air at a constant normal force of 1000 μN by using a pyramidal diamond tip with an included angle of 90° (cube corner) to draw five parallel scratched lines with a length of 10 μm. After the nano-scratching, the specimen was anodically etched under the optimum condition found in the former experiment by using a diamond scriber. Incidently, the mechanical properties of the InP specimen surface were also measured by nano-indentation and nano-scratching. The measured hardness, H, elastic modulus, E, and friction coefficient, μ', were H = 8 GPa, E = 109 GPa and μ' = 0.7.

3. Results and discussion

3.1. Polarization behaviors of the as-received and scratched InP specimens

Fig. 1 shows the potentiodynamic polarization curves measured at a potential sweep rate of 10 mV s^{-1} in 0.5 M HCl for the as-received and scratched InP specimens. It is seen from Fig. 1 that the as-received specimen has one anodic current peak at about 1.7 V (SHE) in the anodic potential sweep, while the scratched specimen has the shoulder in

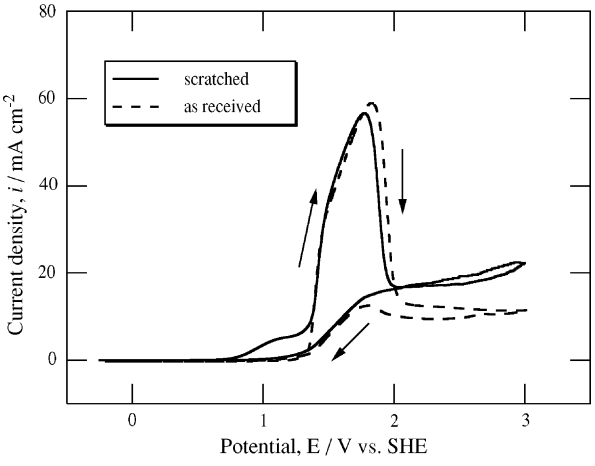

Fig. 1. Potentiodynamic polarization curves measured in 0.5 M HCl for the as-received and scratched InP specimens. Potential sweep rate: 10 mV s^{-1}.