Preparation of Anodic Porous Alumina Mask with Ideally Arranged Holes on InP Single Crystals

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Anodic porous alumina mask with ideally arranged holes was formed on InP single crystals. This process has advantageous in the achievement of nanofabrication with uniformity and reproducibility due to the mask being formed with sufficient adhesion on the InP. The masks formed by this process, was confirmed to applicable for the dry-process mask.

The fabrication of ordered fine patterns of nanometer dimensions on semiconductors is of growing importance for the preparation of the various types of functional nanodevices.[1–3] We have previously reported the process for the ordered nanostructures of InP of III–V semiconductors,[4] which is an important semiconductor for the fabrication of optical devices such as light-emitting diodes, lasers, and photonic crystals[5,6] using anodic porous alumina as a dry etching mask. Anodic porous alumina, which is a typical self-organized material prepared by the anodization of Al, allows the nanofabrication of InP by the use of its self-standing membranes with through holes for the dry etching mask.[4] In the present report, we show the preparation of an anodic porous alumina mask on InP single crystal by the anodization of vacuum-evaporated thin Al, and its application for the preparation of an ordered array of metal nanodots. When compared to the use of the self-standing membrane mask, this process has advantages in achievement of the nanofabrication with uniformity and reproducibility due to the mask being formed with sufficient adhesion on the substrate. In addition, the present process is easy in preparation of the mask, without any problems in the handling of the fragile thin alumina membrane which remains free from breakage. There have been many reports on the fabrication of anodic porous alumina masks on various kinds of substrate using the anodization of the vacuum-deposited thin Al.[7] However, no work has been reported on the preparation of an alumina mask on InP. In addition, the introduction of the pretexturing of Al by imprinting using a mold[8] yielded the anodic porous alumina masks with an ideally ordered hole arrangement on InP single crystals.

The fabrication of an anodic porous alumina mask on InP single crystals was carried out using a process similar to that reported previously.[8] Al of 600-nm thickness was deposited on an InP single crystal wafer [n-type, (100), Sn-doped ($n = 2.5 \times 10^{18}/\mathrm{cm}^3$)] using a vacuum evaporation apparatus (ULVAC EX-201) under the vacuum of 5×10^{-6} Torr. The InP substrate was cooled during vacuum evaporation to suppress the irregularity caused by the growth of the Al crystal. After the evaporation of Al, pretexturing of Al on InP was conducted by imprinting using the SiC mold with ordered convexes at 200-nm intervals under the pressure of 2500 kg/cm^2.

Anodization of Al was conducted under a constant voltage condition of 80 V in 0.5 M phosphoric acid at 16 °C for 15 min, after making lead contact on an Al layer formed on the back surface of the InP. To adjust the pore size, the post-etching treatment was carried out in 5 wt % phosphoric acid at 30 °C. The sample formed through this process was observed using a scanning electron microscope (SEM, JSM-6100).

Figure 1 shows the surface SEM micrograph of the anodic porous alumina mask formed on the InP single crystals. From the view shown in Figure 1, it was confirmed that ideally arranged holes were formed over the alumina mask. The interval and diameter of the holes in the mask were 200 and 130 nm, respectively, corresponding to the textured pattern formed by the imprinting on the vacuum-evaporated Al. For the sample shown in Figure 1, post-etching treatment was carried out in 5 wt % phosphoric acid for 60 min. From Figure 1, it is clear that the convexes formed by the imprinting of Al can act as an initiation site for the hole development during the anodization, and thus generated the ideally ordered anodic porous alumina on the InP single crystal. Cracking due to the imprinting was not observed in either the InP single crystal or the SiC mold.

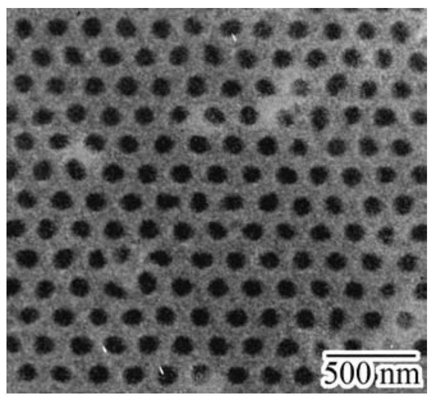

Figure 1. SEM micrograph of anodic porous alumina mask formed on InP single crystal. Post-etching treatment was carried out in 5 wt % phosphoric acid at 30 °C for 60 min.

Figure 2 shows the cross-sectional view of the anodic porous alumina prepared on the InP single-crystal substrate. From Figure 2, it was confirmed that highly ordered straight holes were formed perpendicular to the surface of the substrate. The aspect ratio of the hole depth divided by the hole diameter was approximately 5 in the case of the sample in Figure 2. In the case of the porous alumina mask, which is post-etched in phosphoric acid, the bottom part of the holes called barrier layer could be eliminated entirely, and thus the through holes in mask were yielded.

The through holes could not be obtained without a post-

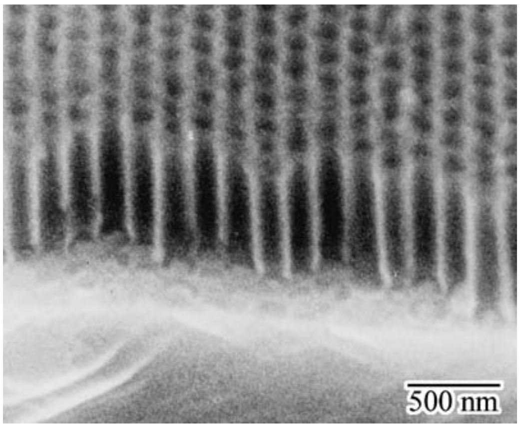

Figure 2. SEM micrograph of anodic porous alumina mask formed on InP single crystal, after post-etching in phosphoric acid.

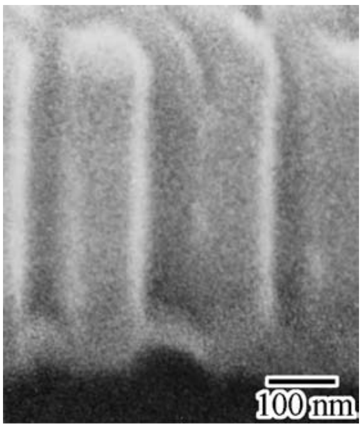

Figure 3. SEM micrograph of anodic porous alumina before post-etching treatment.

etching treatment in phosphoric acid. Before the post-etching treatment, a hemispherical barrier layer was observed at the bottom part of the holes as shown in Figure 3. This hemispherically structured barrier layer at the bottom part of the holes was similar to those observed in the anodic porous alumina on the Si substrate.[8] This structure was easy to be removed by the etching in phosphoric acid because of its unique structure and resulted in the through holes.

After the removal of the alumina mask, it was confirmed that the surface of the InP was unetched and was kept smooth. On the basis of this result, it was confirmed that an InP is stable against anodization and post-etching in a phosphoric acid solution due to the formation of the stable passivation layer on the InP surface that occurs in a phosphoric acid. On the other hand, the dissolution of InP accompanied by breakage of the alumina mask took place during the anodization. This result indicates that adoption of the appropriate anodization solution is important for the reproducible preparation of the alumina mask on the InP substrates.

Figure 4 shows the SEM micrograph of the ordered array of Ag nanodots formed on InP using the vacuum evaporation of Ag

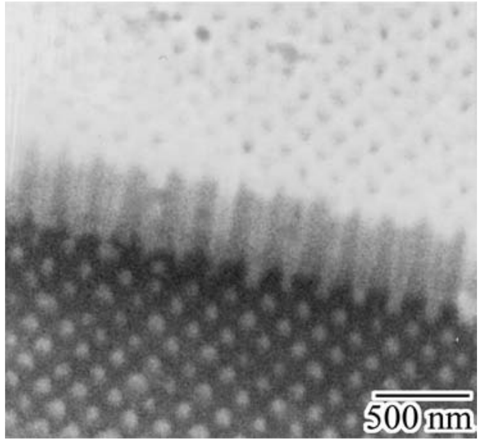

Figure 4. SEM micrograph of the Ag nanodot array formed on InP single crystal. Nominal thickness of vacuum deposited Ag was 60 nm.

through the anodic porous alumina mask. In Figure 4, the formation of an ideally ordered Ag nanodot array was confirmed on the InP single crystal substrate from the area where the mask was partially removed. The periodicity and the diameter of the Ag dots obtained were 200 and 130 nm, respectively. The formation of an almost uniform nanodot array indicated that the post-etching treatment of the porous alumina with phosphoric acid generated the fully etched through-hole in the alumina layer on InP.

An anodic porous alumina mask was formed on an InP single crystal substrate by anodizing of a thin layer of vacuum evaporated Al on the InP. The alumina mask had an ideally ordered hole arrangement formed by conducting a pretexturing treatment of the Al by means of an imprinting process using a mold. The anodic porous alumina masks prepared by the present process on InP have ideally arranged holes with a high aspect ratio. These masks will be useful for the fabrication of various types of nanostructures of InP, particularly for structures with high aspect ratios due to their characteristic feature of high aspect ratios and high resistance for the dry etching.

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