MORPHOLOGY STUDIES OF POROUS GaP, SYNTHESIZED BY LASER-INDUCED ETCHING

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Abstract: *The laser-induced etching (LIE) has been proposed as an alternative technique. This LIE process is used to create GaP nanostructure. The studies of surface morphology of the reconstructed surface etched by laser-induced etching and the etching rate parameters have been investigated. The surface structure, pits diameter and distribution have been illustrated by using a scanning electron microscopy (SEM). Study of the effect of laser parameters on the surface morphology of the etched area such as different laser power densities and irradiation times has been made. Different structures have been produced for porous GaP. It is found that the pore walls become extremely thin and shorter at 12 W/cm^2 power density and 15 min irradiation time.*

Keywords: GaP, morphology, LIE

1.   INTRODUCTION

The opto-electronic application of compound semiconductor materials has attracted extensive research and development activities over the last decade, particularly in the area of quantum functional devices. Porosity has emerged as an effective tool for controlling electronic and optical properties of semiconductor quantum structures.[1,2] Much research on semiconductors is focused on the characterization of surface effects, which strongly affects the properties of a semiconductor. The quantum confinement effects are considered to control the mechanism of luminescence in nanocrystallites. The enhancement of luminescence efficiency is required because the band-to-band transition in the indirect band gap semiconductor material is extremely low. The reduction of size to a few nanometers has been used for the observation of efficient light emission by a modification in electronic, optical and vibrational properties compared to the bulk.[3] Moreover, the absorption edge of band-to-band transitions generally shifts to blue side by the confinement energies of the electrons and holes due to the quantum confinement.[4] When the dimension in a particular direction is less than the Bohr radius (a_B), the motion of the carriers is restricted and the electron and hole wave functions are confined in that direction.

The reported, theoretical and experimental studies, on porous silicon formation span over nearly four decades.[5] The main interest in porous Si resulted from the proposal, made in 1990, that efficient visible light emission from high porosity structures arises from quantum confinement effects as a result of the conversion of the material band gap from indirect to direct and consequently high photoluminescence (PL) efficiency.[6] Several models have been proposed, some of which are functionally equivalent even though the underlying phenomenology is different.

Recently, anodic etching has been effectively used for fabricating porous layers and freestanding membranes of different III-V compounds. Porous III-V semiconductors offer important advantages over porous silicon. These include a possibility of changing the chemical composition and directional etching. Further, III-V compounds exhibit Fröhlich type surface related vibrations with porosity tunable frequencies and efficient second harmonic generation.[7–9] The porous III-V semiconductors, due to their intense luminescence and large non-linear optical response, are promising candidates for fully integrated light sources and frequency converter sub systems.

GaP, which is an indirect band gap (2.26 eV), offered an interesting possibility for obtaining a direct band gap material (2.78 eV) in the form of nanometer size crystalline GaP. Its band gap falls in the green and UV wavelength region and, therefore, is a promising material for the light emitting devices.

Most of studies reported to date concerning the porous GaP layer formation are blue and UV photoluminescence from porous GaP structures prepared by electrochemical anodization of crystalline bulk material. The PL of porous GaP at energies above the band gap of the bulk material has been attributed to quantum size effects.[10–12] Furthermore, porosity-induced intensification of the near-band-edge emission was observed in gallium phosphide. But there is less structural data revealing the dimensionality of the skeleton.[13–14] Many other workers have demonstrated porous GaP photo anodes with significantly enhanced quantum yields around its bulk indirect band gap.[15–16]

The confinement of electrons and holes in quantum wires of GaP in the porous layer was proposed as the origin for the blue and UV emission bands in porous GaP. For the quantum confinement structure in the porous layer, the blue and UV emission is expected to be much stronger than the orange emission from bulk GaP.[17] The optical properties of the porous GaP are different from the properties of the original single crystal. The modification of the properties of GaP could be due to an intensification of the electron-phonon interaction in the submicron to nanometer size structures of the porous layer.[18]

In n-GaP made porous by anodization etching, the photocurrent response within the porous layer indicates an increase in the optical path length in the porous layer. When the absorption length (penetration depth) $(1/\alpha)$ is larger than the thickness of the porous layer, significantly large electron-hole pairs are created in that region.

In semiconductor device fabrication, the wet etching (isotropic and anisotropic) is frequently used. The formation of porous layers is an extreme case of anisotropic etching. The anodic etching is carried out with external bias and the sample is immersed in HF solution. The pore density, dimension and structure of the porous layer depend upon doping density, crystallographic orientation of the surface, etching time and current density. The formation of pore geometry, morphology, growth direction, growth rates and nucleation are fairly well understood for silicon but no clear understanding has emerged for the pore formation and nucleation in III-V semiconductors. Laser-induced etching (LIE) is an alternative technique for controlled dissolution of semiconductors and formation of porous layers with well-defined pore structures. The laser-induced etching technique does not involve external biasing and provides a unique tool for controlling pore structure and dimensions.[19–25] Many semiconductor compounds have been investigated in the porous form. Pore formation has been reported for GaP in many electrolytes.[26,27] A majority of this work has focused on the light emission process, blue and UV-luminescence from porous GaP.[28,29] Though GaP has an indirect band gap structure similar to silicon, the pore structure and pore formation is significantly different.

2.   THE LIE EXPERIMENTAL SET-UP

A simple experimental set-up was used for laser-induced etching (LIE), which consists of a CW argon-ion laser, reflecting mirror, focusing lens and plastic container, as shown in Figure 1. The laser beam (514.5 nm) was reflected by an aluminium coated highly reflecting mirror (99.5%) and focused on to the sample of 1.5 mm diameter by using a suitable quartz lens with focal length of 10 and 5 cm of diameter. This lens was mounted on a micrometer holder for the focusing adjustment. The laser beam power density required for LIE process of GaP was varied up to 12 W/cm^2 and with different irradiation times: 5, 10 and 15 min.

The gallium phosphide wafers (n-type) were rinsed with ethanol for 10 min to clean the surface and then immersed in aqueous 40% wt. HF acid. The immersed wafer was mounted on two Teflon plates in order to allow the current that could pass from bottom to top area (irradiation area) through electrolyte, with suitable power density and irradiation time.

The samples were rinsed with ethanol and dried in air. The porous GaP was formed on the laser-irradiated surface of the samples. The freshly prepared samples were stored immediately in a vacuum chamber under 10^{-3} mbar to avoid contamination. Porous GaP layers had been prepared by laser-induced etching from n-GaP, (100) orientation having carrier concentration $3.7 \times 10^{17} \text{cm}^{-3}$.

Mirror

Argon-ion laser

Focusing lens

Argon-ion laser ($\lambda = 514.5$ nm)
Power density = 1.5–12 W/cm^2
Irradiation time = 5–15 min
Spot size = 1.5 mm
Sample: GaP (n-type)
Etching solution: HF 40%
Rinsing with ethanol
Dry in air

Plastic container

HF acid
GaP wafer
Teflon plates

X-Y Translation

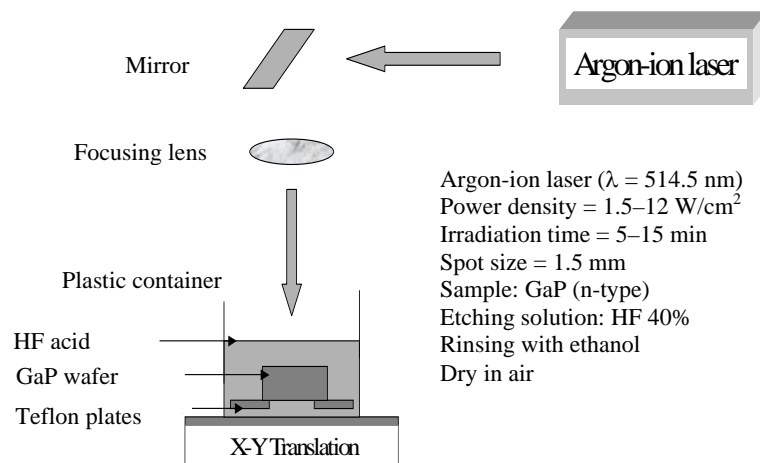Figure 1: The laser-induced etching set-up

3.   SURFACE MORPHOLOGY

Surface morphology of porous semiconductors, in general, is known to be very complicated and depends strongly on fabrication conditions. In this work, we study the surface morphology of porous layers obtained by laser-induced etching of n-type GaP (100) substrates. The morphology of porous gallium phosphide layers changes rapidly with laser power densities and irradiation times.

4.   RESULTS AND DISCUSSIONS

4.1   The Effect of Laser Irradiation Time

The SEM micrographs of twelve representative porous GaP samples etched at different irradiation times were investigated. By keeping the laser power density constant, we studied the effect of varying irradiation time on the morphology of the GaP porous layer.

Three samples were etched at low power density of 1.5 W/cm^2. For small irradiation time of 5 min, the LIE produced pore structure with thick walls. The pore dimension was typically <500 nm and the pores were oriented along the (111) direction. The pore structure was not clearly defined as shown in Figure 2(a). On increasing the irradiation time to 10 min, the pore structure became slightly disordered as shown in Figure 2(b).The increased irradiation time decreased the pore wall dimension to approximately 250 nm, though the etched area was irregular; the structure was still oriented along (111). On increasing the irradiation time further up to 15 min, as shown in Figure 2(c), there was an evidence of deep pores existence with clearly defined broken pore walls along the (111) direction. The pore walls were approximately 200 nm thick and some of the pore walls showed extremely thin tips at the top. This indicated that the pore walls had non-uniform thickness at the higher irradiation time.
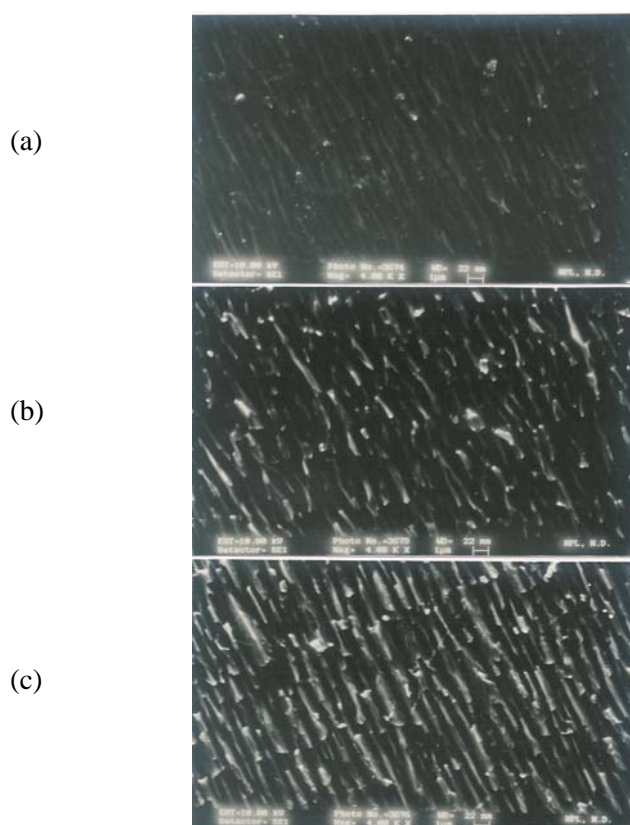
(a)

(b)

(c)

Figure 2: SEM images of porous GaP synthesized by LIE at laser power density 1.5 W/cm^2 for (a) 5 min, (b) 10 min, and (c) 15 min irradiation time

When the power density increased to 3 W/cm^2, lateral structures were clearly visible even with small irradiation time of 5 min, as seen in Figure 3(a). The pore structures apparently always grow along the (111) direction irrespective of power density of laser and the irradiation time. The higher power density reduced the wall thickness to 100 nm though the structure remained fairly regular.

On increasing the irradiation time to 10 min, there was an increase in the pore density and decrease in pore wall thickness to 80 to 100 nm as shown in Figure 3(b). The image of Figure 3(c) showed the structure of the porous layer when the GaP substrate irradiated for 15 min, which revealed that the longer irradiation time created porous layer with highly regular lateral structure along the (111) directions with pore dimension of 50 to 80 nm. It appeared that the high laser power density along with long irradiation time led to dissolution of already formed structure in the porous layer due to the availability of high density of electron hole pairs at the semiconductor-electrolyte interface.

When the power density was increasing up to 6 W/cm^2 at small etching time of 5 min, the etched surface onset of pore structure with small pits were irregular in shape and size, shown in Figure 4(a). For the etching time of 10 min, the structure of porous layer was more regular broken wire-like shape oriented along the (111) direction with lateral separation of 150 nm, shown in Figure 4(b). At 15 min etching time, one can see in Figure 4(c) that the disorder set in. The pore layers consisted of crystalline GaP with pores aligned in distinct crystallographic directions. The surface shows lateral structures in the (111) directions. The pore dimension was ~100 nm. The pore wall was probably insoluble GaF$_3$.3H$_2$O, while the various gallium and phosphorous oxides, as well as the relevant phosphorous was soluble in aqueous solutions of low pH 30.

For the laser power density of 12 W/cm^2, a well-defined wire-like pore structure was formed even for 5 min irradiation time due to the large density of hole supplied at the semiconductor-electrolyte interface. The long wires running parallel to (111) direction had various sizes. Therefore, the regular structures had been synthesized for 100 nm pore dimension under these parameters as can be seen in Figure 5(a). At longer irradiation time of 10 min, the pore structure had grown deeper with thinner pore walls. Some of the pore walls are 20 to 50 nm in dimension as shown in Figure 5(b). Further increase in the irradiation time to 15 min. led to the pore propagating deep into the substrate and the pore walls becoming extremely thin, in the range of 10 to 50 nm as can be seen in Figure 5(c), the large portion of the walls was also etched away and pore walls became shorter. At much higher laser power density the pore structure became disordered and a hole is created in the substrate.
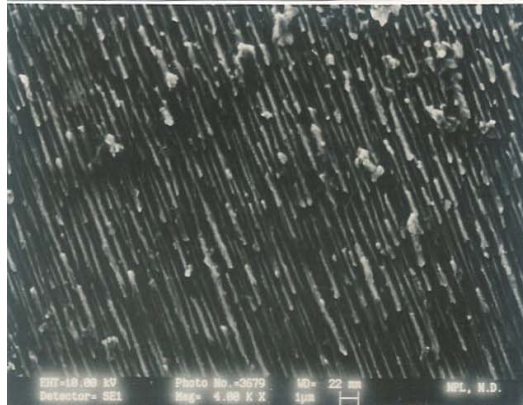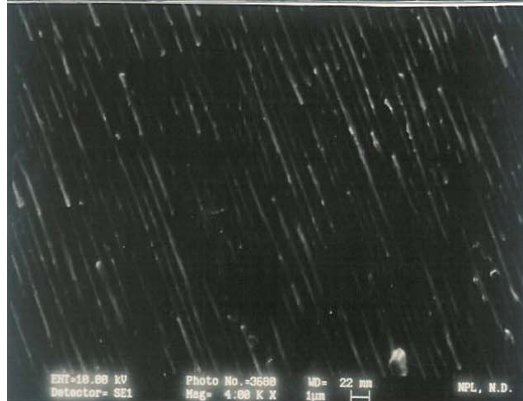
Figure 3: SEM images of LIE synthesized porous GaP at laser power density of 3 W/cm^2 for (a) 5 min, (b) 10 min, and (c) 15 min irradiation time

(a)

(b)
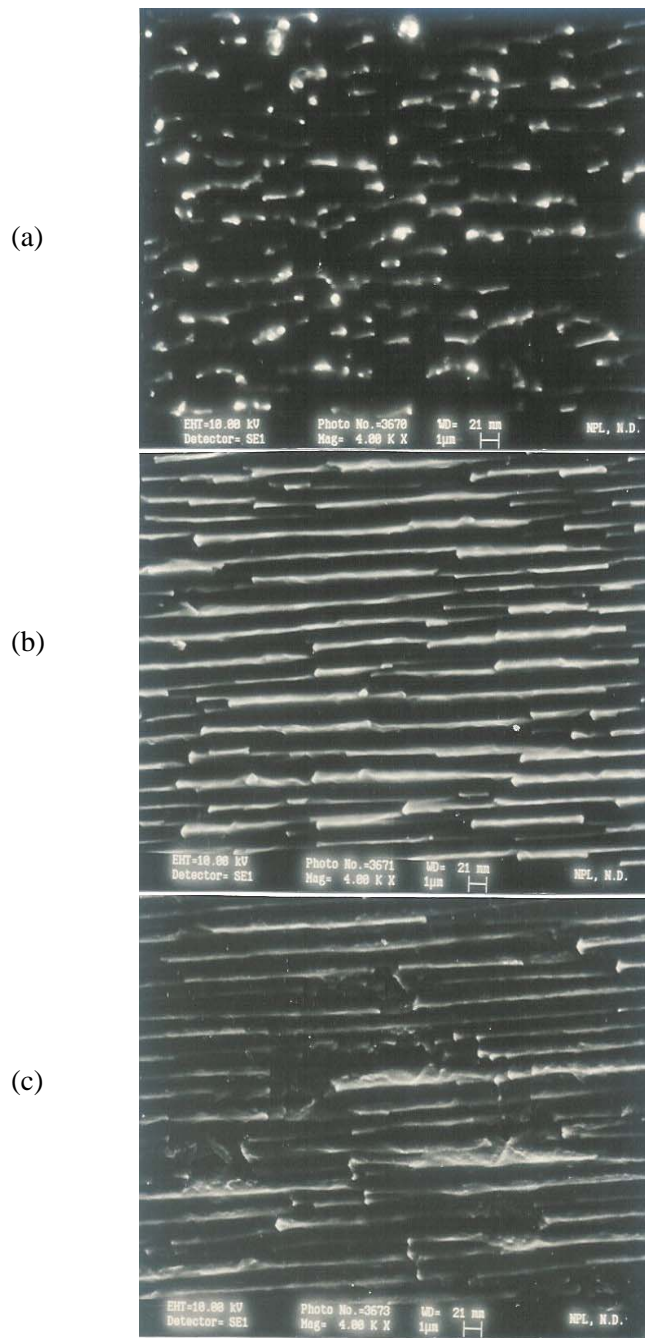
(c)

Figure 4: SEM images of LIE synthesized porous GaP at laser power density of 6 W/cm^2 for (a) 5 min, (b) 10 min, and (c) 15 min irradiation time
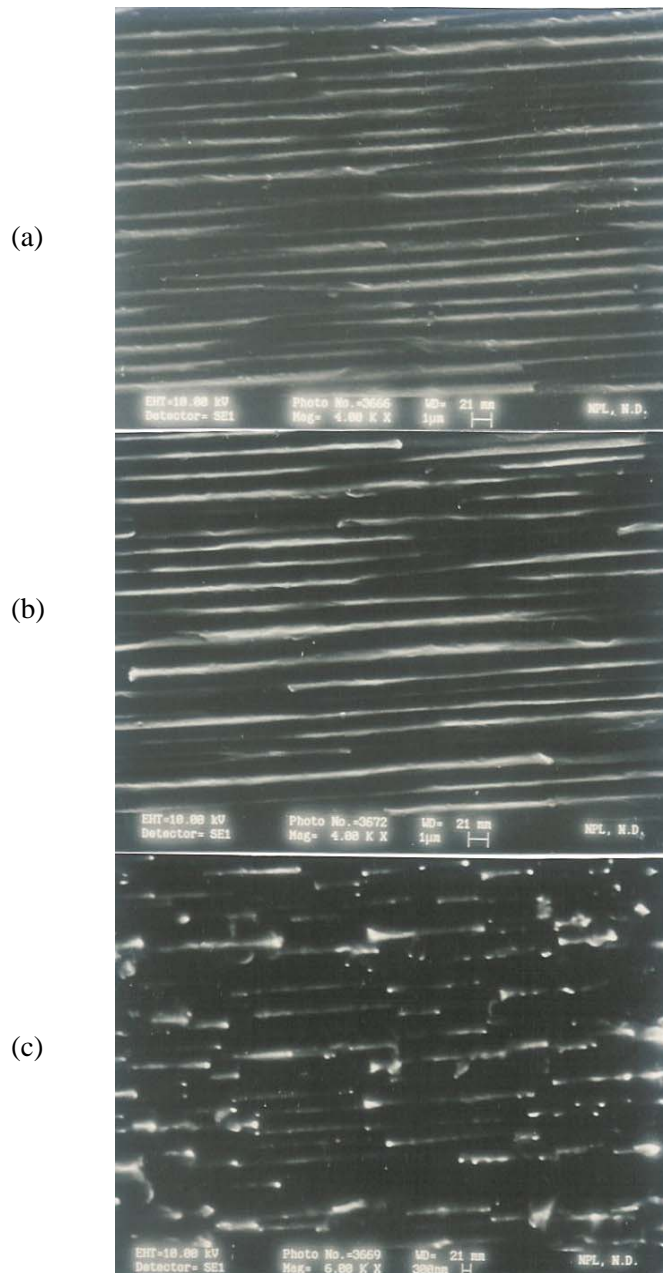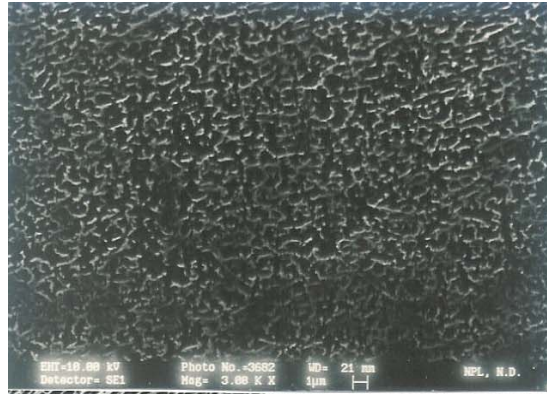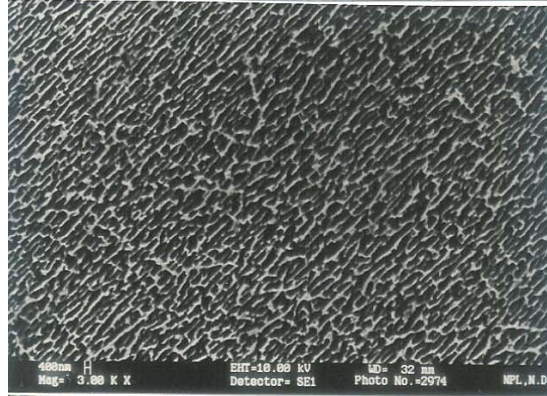
(a)

(b)

(c)

Figure 5: SEM images of porous GaP synthesized by LIE at laser power density
of 12 W/cm^2 for (a) 5 min, (b) 10 min, and (c) 15 min irradiation time
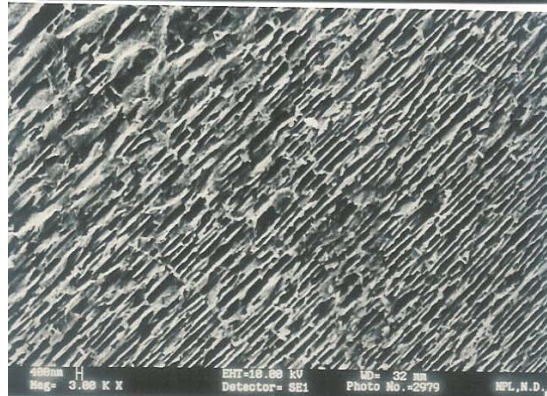
(a)

(b)

(c)

Figure 6: SEM images of porous GaP produced by LIE at 12 W/cm^2 for (a) 5 min, (b) 10 min, and (c) 15 min with HF + ethanol as electrolyte

4.2   The Effect of Electrolyte Concentration

The GaP substrate was immersed in HF acid 40% diluted by ethanol 50% under different irradiation times 5, 10 and 15 min and with a fixed power density of 12 W/cm^2.

It can be seen from the SEM micrographs that the surface morphology and pore structure of the etched GaP samples are quite different from sample etched with concentrated HF electrolyte. Figure 6(a) shows the morphology of porous GaP sample that was irradiated for 5 min. The pore morphology was random with no sign of any preferential etching. There were coarse features in the micrometer range and, on top of them, fine features with size in the range below 250 nm. It appears that the photochemical etching produces a bimodal effect in the crystal size distribution with coarse structure supporting the fine nanometer size structure.[8, 11–12, 15, 28–33]

With an increase in the irradiation time, the pores grew selectively along a preferred crystallographic direction. On increasing the etching time to 10 min, illustrated by Figure 6(b), the pore structure was more oriented, while for 15 min irradiation time, shown by Figure 6(c), the orientation probably change from (100) to (111) direction, under same etching conditions. The structures were more uniform and the pore dimension was around 150 to 200 nm. The pore diameter was the same throughout the porous layers and the GaP remaining between the pores was crystalline. The lighter areas corresponded to the GaP and the dark parts to the pores. No lateral structures could be seen in these samples but the SEM had revealed a cylindrical or wire-like geometry and the charge carriers confined in such wires would result in an increase of the band gap energy due to the quantum confinement.

5.   DISCUSSION

In GaP, the etching was preferentially along the (111) direction. Similar surface morphologies had also been observed in the photochemical etching of n-InP (100) where the preferential growth direction was along the (011) axis.[34] The SEM micrographs revealed that the pores grow in the (111) directions from gallium to phosphorous denoted as the (111) direction, similar to that in GaAs.[30] The chemical reaction of the hole with phosphorous was stronger than with gallium due to high reactivity of phosphorous. At the onset of etching, there were disjointed lateral structures. When the irradiation time was further increased, the pores become randomly oriented and their size reduced with an increase in the power density. This was due to random etching caused by the very high density of holes presented at the GaP surface. It could be inferred that the porosity was

initially found to increase with increasing etching time, but there existed an optimum etching time beyond which the porosity decreased and randomization of the pores set in.

On further increasing the power density, the pore widened and the morphology became highly regular. The pores were all aligned along the (111) preferential direction. It was also observed that as the power density for etching was increased, the optimum etching time decreased. Furthermore, as the pore size increased, the wall thickness decreased and the pore walls were well defined. It could be concluded that the regular oriented nano-size structures could be etched on GaP substrate by laser-induced etching. Selecting suitable power density and irradiation time could control both the size and the shape of these structures.

6.   CONCLUSION

The processing of laser-induced etching was accomplished by first absorbing band-gap photons in semiconducting electrode immersed in an appropriate liquid electrolyte. Electron-hole pairs were created in the semiconductors, which then separated in the space charge layer of the semiconductors. The etching proceeded through trapping of valence band holes in surface bands. The electrons in the conduction band created at the surface can gain sufficient kinetic energy in a large power density to generate new electron-hole pairs upon impact with an atom thus breaking lattice bonds. The valence band electrons at the surface could be tuned to the conduction band if photons with large energies were present, thus creating free holes in the valence band also. The crystallographic orientation in anisotropic etching, determined the density, dimensions and shapes of pores. The technique of laser-induced etching could be successfully adopted to synthesize GaP nanoparticles. Also, if the laser energy was tuned, then the etched structure could be created deeper into the substrate due to variation in the penetration depth.

7.   REFERENCES

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