
Laser-induced etching of Cr–O doped GaAs and wavelength dependent photoluminescence

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Abstract

The laser-induced chemical etching mechanism of Cr–O doped GaAs (1 0 0) substrate in 40% HF-H2O solution is explained by the generation of e–h pairs through defect states in the presence of sub-bandgap photon illumination by using a Nd:YAG Laser (λ ∼ 1.06 μm). The central feature of the laser etching technique is pits initiation by surface defects. The etched GaAs samples are characterised by photoluminescence (PL) spectroscopy. The PL spectrum shows the formation of GaAs nanostructures and chemical reaction products. The shape of the PL band (1.3–1.8 eV) obtained from the top surface depends on the penetration depth of excitation wavelength. An estimate of the nanocrystallites sizes present in the laser etched layer is obtained by quantum confinement model.

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1. Introduction

Nanometer size III–V semiconductors is promising materials for optoelectronic devices since quantum confinement in such materials modifies the band structure and leads to unique optical properties. Micro- and nanocrystals can be fabricated by laser-induced etching. It is a topic encompassing light-induced chemical reaction of semiconductors in contact with liquids. The light-induced minority carriers in semiconductors can stimulate spatially selective or material-selective etching and deposition reactions. An important advantage of this form of etching, which is purely chemical in nature, is that it does not rely on the bombardment of massive particles to achieve etching and thus damage is not incurred. On irradiating semiconductors in an etchant with a laser, the light-induced chemistry occurs within the laser-illuminated area and localised dissolution of semiconductors takes place due to etching. The mechanism and cause of the localised nature of the pore formation process, as well as the factors affecting etching, i.e. etchant, laser photon energy and crystallographic orientation of the sample surface, etc., are still poorly understood. Many investigators [1–9] have developed numerous etchants for GaAs but most of the previous reported data on the GaAs etching dealt mainly with the photo-electrochemical etching. The exact mechanism of a laser-induced etching, where laser photon energy is less than the band gap energy of GaAs (1.42 eV) and post-etched photoluminescence has not been studied at length. This is mainly due to the complexity of the etching mechanism that is influenced by the type of dopant, degree of doping, presence of defects and etching condition, etc. Several authors [1–4] have discussed the anodic etching behaviour. Gerischer and Bunsengesellschaft [5] has described electrochemical behaviour of n-type semiconductors under illumination. Recently, Beji et al. [6] have produced porous GaAs from heavily doped p-type GaAs by a electrochemical anodic etching. The porous layer exhibits PL bands between 1.4 and 1.9 eV. Oskam et al. [7] have also studied the formation of porous GaAs in HF solution by electrochemical etching. They found that the pore density, pore dimension and the structure of the porous layer depend on the doping density and crystallographic orientation of the surface. Svorcik et al. [8,9] have reported a laser-induced etching on n-type GaAs in H2SO4/H2O2/H2O2 solution that is higher than the band gap of GaAs. Recently, we have shown that the GaAs nanocrystals can be fabricated by a laser-induced etching using a Nd:YAG Laser [10].
Few PL studies dealing with nanocrystalline GaAs prepared by laser-induced etching can be found in the literature. The PL data provide important information concerning crystallinity, size and size distribution in the samples. The broad PL band from the etched nanocrystalline GaAs is explained under the assumption that the etched GaAs contains a distribution of nanocrystallites with different sizes [10–13]. The PL peak position and shape can be related quantitatively with crystal size in the electron confinement model. The excitation wavelength dependence is not considered in this model. However it has been found that it strongly affects the PL shape in the laser etched samples because different wavelengths will have different penetration depths. Therefore, different excitation wavelengths can be used to examine the different etched GaAs layers.

The present study focuses on the investigation of a laser-induced etching using a photon energy less than the band gap energy ($E_G \sim 1.42$ eV of crystalline GaAs) and pore formation mechanism on semi-insulating GaAs. Chemical conditions, under which local dissolution and pore formation occurs, are also discussed. The PL spectra are measured at same point with different excitation wavelengths in the etched GaAs samples. It shows different line shape of PL spectra. The results are analysed using confinement model [11].

2. Experimental procedure

A commercially available Cr–O doped GaAs (1 0 0) wafer with resistivity of $10^7$ $\Omega$ cm was immersed in 40% hydrofluoric acid in a plastic container and was supported on two Teflon plates. The Cr content in the sample was roughly to 1 wt. ppm. Photochemical etching was done by using a Nd:YAG ($\lambda \sim 1.06$ µm, Quantronix, model 331) Laser in CW mode. The beam was focused to a circular spot of 1.5 mm diameter. The sample was irradiated with laser power density 30 W/cm$^2$ for the duration of 30 min to etch above mentioned GaAs wafer. After etching, the sample was rinsed with ethanol and dried in air with filtered N$_2$. Detailed schematic diagram of experimental set-up and procedure are described in [10]. The PL spectra were recorded by employing a spectroscopic system constituting of a photomultiplier tube (R943-2), an amplifier-discriminator assembly, a photon counter, a computer and an argon-ion laser (COHERENT, INNOVA 90-5). The surface morphology of the etched sample was studied by SEM (Cambridge Instrument, Stereoscane 360).

3. Results and discussion

3.1. Laser-induced etching and surface morphology

Our sample GaAs is doped with two species Cr and O, where chromium creates a donor state at 0.4 eV and oxygen, on the other hand, creates an acceptor state $\sim 0.63$ eV within the forbidden gap for moderate doping. Both the energy levels are measured from the bottom of the conduction band [14]. Due to compensation with the presence of both types of impurities, the Fermi level is pinned near the intrinsic Fermi level. The GaAs material is becomes highly resistive, i.e. semi-insulating in all samples. The laser beam of wavelength $\lambda \sim 1.06$ µm (1.16 eV), used in this etching process, is not sufficient to excite the e–h pairs through band-to-band transition in the semiconductor depletion region near the interface. However, etching has been taken place in our sample. The evidence of the redox phenomena, i.e. the formation porous structure is observed by SEM micrograph. Since hydrofluoric acid alone does not react with GaAs, which is free of surface oxide film, it raises a fundamental question on the etching phenomena in our case. It is to be noted that the laser beam power used in our experimental is extremely low, even the photons of higher harmonic generation in the sample all also ruled out. Therefore, a model is proposed here to explain the photo-induced etching mechanism of semi-insulating GaAs.

Any impurity or lattice defect can serve as a generation/recombination centres if it is capable of receiving a carrier of one type and subsequently capturing the opposite type of carrier, thereby generating/annihilating the e–h pairs. One such example is demonstrated in Fig. 1. $E_t$ represents one defect state below $E_G$ at equilibrium and therefore, is substantially filled with electrons. The defect state will be filled or partially filled depending upon the relative positions with respect to the extrinsic Fermi level position. Excess e–h pair generation occurs in two steps: (A) hole emission and (B) electron emission. It is important to note that the first event is equivalent to an electron excited from $E_G$ to the conduction band creating a hole in the defect state. In the second event, the hole is transferred to the valence band by an electron excitation from the valence band to $E_t$. When both these events occur simultaneously, the defect state is back to its original state. The photogenerated holes drifts to the interface and the electron is swept away from the interface due to the electric field in the interface. The laser light having photon energy less than band gap falls upon the surface and interacts with the defect states created by impurities and

![Fig. 1. Capture processes at a defect level: (A) hole emission at a filled defect state, (B) electron emission at an empty centre.](image-url)
It creates the e–h pairs. The electric field produced at GaAs/electrolyte interface causes the holes to drift to the interface and consequently etching will start by redox process. In support of above mention discussion the chemical reaction can be given \[8,9\] by

\[
\text{GaAs} + 6h^+ \rightarrow \text{Ga}^{3+} + \text{As}^{3+} \quad (1)
\]

\[
\text{GaAs} + 3e^- \rightarrow \text{Ga}^0 + \text{As}^{3-} \quad (2)
\]

In GaAs, band bending in the space charge region moves holes toward the surface where, they initiate etching and pit formation take place in GaAs. Pits initiation is prerequisite criteria for pore formation in the GaAs substrate. A pit will be formed at a point on the surface where the dissolution rate is enhanced. The most important etch pit is the one associated with the point of emergence of a dislocation on the surface. The GaAs is well known to have moderate to high density of dislocation even in its purest form\[15\]. The interconnection will lead to an extra free bond at the surface, which increases chemical activity and starts avalanche mechanism at surface defects. The localised etching process induces a pit, which will have increased electrical field strength at its tip and causes the pore size to propagate\[16\]. Furthermore, the dissolution process is controlled by the flow of carriers across the semiconductor/electrolyte interface.

Fig. 2 shows a SEM image revealing the general view of surface morphology of the etched GaAs wafer prepared using laser-induced etching using Nd:YAG Laser. The bright grains of material with range of size <300 nm on the top of a dark film are observed. These crystallites are distributed non-uniformly. Due to limitation of resolution in the SEM, the etched surface could not be fully resolved for further small structures. The average depth of the etched layer is determined by optical microscope about 3 \(\mu\)m. Recently, Simkienė et al. \[17\] have shown in the cross-sectional SEM micrograph of the GaAs:Cr sample prepared by anodic etching. The top layer (thickness 0.24–0.4 \(\mu\)m) consists of grain sizes 300–500 nm and bottom layer consists of porous layer of GaAs nanostructures. Our SEM, which shows only top layer, is quite similar to \[17\].

3.2. Excitation wavelength dependent photoluminescence

Fig. 3 shows the PL spectra of the etched and unetched samples recorded at 20 K. For the etched samples, PL spectrum shows two distinct bands in Fig. 3(b). Firstly, band-A, is a PL spectra from 1.3 to 1.9 eV, and the maxima of the PL peak energy appears at 1.6 eV (\(\lambda \sim 774.8\) nm). It is blue-shifted roughly 100 meV in comparison to bulk unetched GaAs. It has a broad luminescence, FWHM roughly 300 meV with a tail towards higher energy. Secondly, band-B, is PL spectra from 1.9 to 2.3 eV and maxima appears around 2.18 eV (\(\lambda \sim 568.7\) nm). The PL intensity of band-B is almost double the intensity of the band-A and is symmetrical in nature. To check the origin of above-mentioned bands, we have recorded the PL spectra with the different excitation wavelengths. On changing excitation wavelength from 457.9 to 488 nm, the penetration depth of laser light increases from 0.2 to 0.5 \(\mu\)m. Therefore, we will be getting the PL spectra from the top etched layer as well as from slightly deeper inside the GaAs etched layer. The effect can be seen in the PL spectra in Fig. 3(c). For excitation wavelength 488 nm, the PL spectra from 1.3 to 1.9 eV can be further divided into two bands, band-A1 (maxima of band at 1.6 eV) and band-A2 (shoulder of band around 1.8 eV) as shown in Fig. 3(c) more clearly. On the contrary, the PL peak position energy and shape of the band-B remains the same. These data indicate that both bands have different origin.

Analysis of the PL spectra for a band-A: the PL between 1.6 to 1.8 eV of GaAs based nanocrystalline materials are described in the literature \[18–21\] as nanocrystals size-dependent. We also observed the PL around same position. It has been proposed that the electronic confinement within nanometer size crystallites leads to a blue shift of the band gap to the visible region and a distribution of crystallite sizes may be responsible for the broad band PL \[11,12\].
size of GaAs nanocrystallites can be determined by a model proposed by Suemoto et al. [11], assuming that each particle constituting etched GaAs gives a sharp luminescence. For a size distribution function $D(R_g)$, the PL intensity $S(E)$ can be written as:

$$S(E) = \text{cwt}(E_{\text{exc}} - E)D(R_g) \frac{R_g}{\Gamma/E - E_g^0}$$

where $R_g$ is the crystallite radius defined by $R_g = (g/(E - E_g^0))^{1/2}$ and $n = 2$. The $E_g^0$ is the gap energy of bulk GaAs. The $(E - E_g^0)$ is inversely proportional to the square of radius of the crystallites. The coupling constant $g$ is in eV $(\AA)^2$, while $E_g^0$ is 1.42 eV at room temperature. The $c$ is a constant, which includes an intensity of light source at excitation energy $E_{\text{exc}}$. The $a(E_{\text{exc}} - E)$ is the absorption coefficient. The function $a(E)$ can be reduced to a simple form such as $a(E) = a_1 + a_2E^2$, where $a_1$ and $a_2$ are constants. The function $D(R)$ is taken here as a Gaussian distribution function $[\exp(-R^2/(\sigma^2))]$. The PL spectrum excited by higher wavelength 488 nm shows two bands, a maxima at 1.6 eV and a shoulder around 1.8 eV in Fig. 3(c). Kanemitsu et al. [20] have reported the similar PL spectrum of GaAs nanocrystals which consists of two bands related to free- and bound-exciton. From resonantly excited PL spectra and luminescence–hole burning spectra they have shown that the higher energy band is due to delocalized-excitons (free-exciton) emission in GaAs nanocrystal and lower-energy band is due to the bound-exciton emission. We have also observed the similar PL spectrum from our laser etched GaAs samples. For the free-exciton and the bound-exciton, we assume, two Gaussian distribution functions and each one is fitted with Eq. (3). The calculated excitonic energy spectrum for the free-exciton and the bound-exciton are shown by dotted line in Fig. 4(a). Finally, we take convolution of both the excitonic spectrums. It can fit our experimental data of Fig. 4(a) and various fitting parameters including size distribution are given in Table 1. The theoretically calculated shapes of PL bands are drawn as continuous curves in Fig. 4(a).

The experimental data (solid up-triangle) has a reasonably good fitting with the theoretical results. Therefore, the analysis using Eq. (3) leads us to the conclusion that the etched surface constitutes nanocrystallites of size distributions in the range 3.5–4.6 nm. Similarly, for other laser excitation wavelengths 476.5 and 457.9 nm, the PL spectra of the same sample are shown in Fig. 4(b) and (c), respectively. The sample shows a broad luminescence band with peak position energy at 1.6 eV for both the excitation wavelengths. On changing excitation wavelength from 488 to 476.5 nm, the penetration depth of the laser light decreases [22] and the top layer of etched GaAs is excited. Consequently, the PL for the free-excitons and the bound-excitons become closer and comparable to each other as shown in Fig. 4(b).

The fitted results of the PL spectra are given in Table 1. Analysis of the PL spectra for a band-B: the origin of band-B may be related with the chemical reaction by products created on the surface during oxidation. Fig. 3 shows the maxima of the PL peak at 2.18 eV (568 nm). Schmuki et al. [3] have reported the visible luminescence (~540 nm) when GaAs is exposed to an anodic bias in aqueous HCl.

<table>
<thead>
<tr>
<th>Band</th>
<th>Excitation wavelength (nm)</th>
<th>Theoretical</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>488</td>
<td>4.6</td>
<td>5</td>
</tr>
<tr>
<td>A2</td>
<td>488</td>
<td>3.5</td>
<td>5</td>
</tr>
<tr>
<td>A1</td>
<td>476.5</td>
<td>4.8</td>
<td>5</td>
</tr>
<tr>
<td>A2</td>
<td>476.5</td>
<td>3.6</td>
<td>5</td>
</tr>
<tr>
<td>A1</td>
<td>457.9</td>
<td>5.4</td>
<td>5</td>
</tr>
<tr>
<td>A2</td>
<td>457.9</td>
<td>4.0</td>
<td>5</td>
</tr>
</tbody>
</table>

The $\sigma$ is the standard deviation of the Gaussian distribution function (DF) used in Eq. (3).
emit a luminescence peak near 2.2 eV [18], which coincides not only of GaAs nanostructure but also the facetted As$_2$O$_3$ case. We believe that the laser-induced etched layer consists the conversion of As(V) to As(III) is highly probable in our with our PL data. Since etching was conducted for 30 min, nanocrystals may contain Cr or O impurities acting as laser-induced etching of Cr is higher than free-exciton. Our samples are fabricated by fi
cates that con...

457.9 nm, we penetrate only the top layers of etched sample found that the variation of PL peak energy position is more upon the excitation wavelength. For free-excitons, it is a straight line. It implies that this band does not depend

depends upon excitation wavelength. It is found that the free-exciton are more than band gap. The central feature of the laser-induced etching in HF solution is the pits initiation and subsequently pore formation and propagation. The surface defects are the most likely reason for the formation of pitted structures within GaAs substrate. The surface and its composition were characterised by photoluminescence spectroscopy. The appearance of luminescence bands at 1.6 eV blue shifted by more than 100 meV with large width establishes the forma-
tion of GaAs nanostructure in the porous layer. The PL spec-
tra show the free-exciton and the bound-exciton emission of quantum-confinement GaAs nanocrystals fabricated by laser-induced etching. The shape of PL depends upon exci-
tation wavelength. It is found that the free-exciton are more on top layers in comparison to deeper layer in laser etched GaAs nanocrystals. The present excitors-related PL study on the confinement effect will be useful for further investiga-
tion of physical properties (e.g. electron–phonon interaction and scattering) of GaAs nanocrystals in the applications of the electronic devices.

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