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Etching temperature dependence of optical properties of the electrochemically etched *n*-GaAs

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ABSTRACT The GaAs granular films have been prepared by electrochemical anodic etching of *n*-GaAs in HCl electrolyte at different etching temperatures. The microstructure and optical properties of the films were investigated by micro-Raman spectrum, atomic force microscopy (AFM) and photoluminescence (PL) spectroscopy. Raman spectra reveal marked redshift and broadening, which could be explained by phonon confinement model. Results show the GaAs nanocrystalline films have formed during the anodic etching process under certain chemical conditions. Two “infrared” PL bands at ~ 860 nm and ~ 920 nm and a strongly enhanced visible PL band envelope around 550 nm were observed in the film prepared at etching temperature of 50 °C. The “green” PL band envelope is attributed to both quantum confinement in GaAs nanocrystals and PL of Ga₂O₃ and As₂O₃. The results reveal that the energy band structure of GaAs granular films is closely related to the etching temperatures.

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1 Introduction

In recent years the localized dissolution of semiconductors has attracted a great deal of interests because of the discovery of the visible light emitting properties of porous silicon and its potential applications in light emitting devices such as optoelectronic switches and logic gates [1, 2]. Anodic oxidation, due to its good features such as low temperature, the simplicity and low processing costs, has been an effective way to fabricate porous structure semiconductors, such as SiC [3], InP [4–6], GaP [7–12], and GaAs [13–16].

GaAs is an important semiconductor with a direct band gap (1.424 eV) and a large exciton Bohr diameter (19 nm) [17]. A great deal of interest has been generated in both the etching of GaAs and formation of an oxide layer on its surface due to their unique optical properties and various applications particularly in electronic devices and in dry/wet solar cells [18]. M. Hao et al. [19] have formed porous GaAs using a two-step anodization process. The rate and product of GaAs oxidation depend on several factors: illumination,

the pH of the electrolyte [18]. The rate of these oxides increase by illumination because the carriers involve in oxide of GaAs are the valence bond holes. Working in strongly alkaline solutions prevents the growth of oxide layers but causes lattice dissolution, while working in neutral and acidic electrolytes favors oxide growth. Lots of works have been done to research the photoluminescence (PL) property of porous GaAs [13–16, 19], and some very interesting PL properties have been observed. Porous GaAs produced in HF solution using *p*-type GaAs exhibits an “infrared” PL band and a “yellow” PL band [14]. And porous GaAs fabricated in HCl solution using *n*-type GaAs shows an “infrared” PL band and a “green” PL band [15]. Both the “yellow” PL band and the “green” PL band were explained by the quantum effect in nano-sized GaAs crystallites. However, there is no report about the relationship between the optical properties of electrochemical etched GaAs and etching temperature, and the origin of “green” PL band is still not completely understood.

In our work, the GaAs granular films have been prepared by electrochemical anodic etching of *n*-GaAs in HCl electrolyte at different etching temperatures. The microstructure and optical properties of anodized GaAs are discussed in detail by using micro-Raman and temperature dependence PL spectra. The broad and asymmetric Raman peaks are observed in the anodized GaAs, which could be explained by phonon confinement effect. It is found that the GaAs granular films prepared at etching temperature of 50 °C reveals strongly enhanced visible photoluminescence, which could be attributed to both the quantum confinement in GaAs nanocrystals and PL of Ga₂O₃ and As₂O₃.

2 Experimental

The wafers used in this study are *n*-type GaAs(100) wafers doped with $2 \times 10^{18} \text{ cm}^{-3}$ Te and the area of each wafer is $0.5 \times 0.5 \text{ cm}^2$. Prior to each experiment, the samples were degreased with acetone and extensively rinsed with deionized water and then blown dry in N₂. The samples were then pasted to the center of circular sheet with a copper by silver pastern. The exposed part of the circular sheet was covered with insulating paint. An o-ring was pressed against the sample when the circular sheet copper was screwed down in a teflon electrochemical cell as the anode. Accordingly graphite was used as the cathode, and the electrolyte was

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Sample group	Etching solution	Etching potential (V)	Etching temperature (°C)	Etching time (min)
A	HCl (0.1 M)	7	30	10
B	HCl (0.1 M)	7	50	10
C	HCl (0.1 M)	7	70	10

TABLE 1 Sample data

hydrochloric acid. All solutions were prepared from analytical grade chemicals and deionized water. Then the electrochemical etching carried out in the 0.1 M HCl electrolyte for 10 min under the constant anodizing voltage of 7 V and electrolyte temperature of 30 °C, 50 °C and 70 °C, respectively. The sample data and preparation conditions are summarized in Table 1.

The biasing potentials as well as the polarization curve were recorded with an electrochemical analysis system (CHI618B). The AFM imaging was performed in air using a Digital Instruments Nanoscope IIIa in tapping mode. The Raman and PL spectra were recorded by a spectrometer with a liquid-nitrogen cooled charge coupled device detector, attached to a metallographic microscope. The Raman and PL excitation light sources were the 514.5 nm line of Ar⁺ laser and the 325 nm line of ultraviolet laser, respectively.

3 Results and discussion

Figure 1 shows the Raman spectra at room temperature of the four samples (untreated GaAs, sample A, B and C). The Raman spectrum of untreated GaAs contains both the transverse optical (TO) band and longitudinal optical (LO) band. The peak positions of them are 272 and 295 cm⁻¹, respectively, which are coincident with the reported results [20]. For sample A and C, the two peak positions are almost consistent with those in untreated GaAs. While the intensities of TO bands and LO bands increase in comparison with untreated GaAs, which could be explained by the coupling of both the incident and the scattered fields with the low-order-structure resonance on the roughly etched surfaces [21]. However, for sample B, which was prepared by a potential of 7 V in

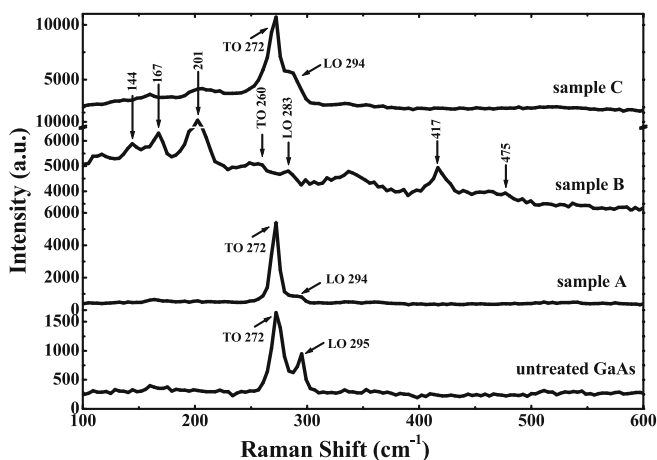


FIGURE 1 Raman spectra recorded at room temperature for different samples

0.1 M HCl at 50 °C, the two Raman peak positions have been shifted down by nearly 12 cm⁻¹ with respect to those in untreated GaAs. And the shapes of the LO and TO bands become markedly broader and asymmetric towards the lower energy tail in comparison with the usual sharp nature of untreated GaAs. Moreover, except for the two Raman peaks, some obviously new Raman peaks at 144, 167, 201, 417, and 475 cm⁻¹ are observed.

The results [22] show that the smaller the size of crystalline particle is, the bigger the frequency shifts and the more asymmetric and the broader the peak becomes. So, from the characteristics of the Raman peaks (TO and LO) of sample B, it can be deduced that the nanocrystalline GaAs has formed in the etching layer of the sample B during anodic etching process. In order to estimate the size of GaAs nanocrystal particle, we fit the LO band of sample B with the “spatial correlation” model [23]. The Raman intensity, $I(\omega)$, at a frequency ω , can be obtained from the following equation:

$$I(\omega) \propto \int_0^1 \exp\left(\frac{-q^2 L^2}{4}\right) \times \frac{d^3 q}{[\omega - \omega(q)]^2 + (\Gamma_0/2)^2}, \quad (1)$$

where q is expressed in units of $2\pi/a$, a is the lattice constant of GaAs (0.564 nm), Γ_0 is the natural line width (full width at half maximum), L is the crystallite size, and $\omega(q)$ is the phonon dispersion curve. Based on an one-dimensional linear-chain model, the dispersion curve $\omega(q)$ of the LO phonon satisfies the following equation for GaAs [24]:

$$\omega^2(q) = A + \{A^2 - B[1 - \cos(\pi q)]\}^{1/2}, \quad (2)$$

which with $A = 4.14 \times 10^4$ cm⁻² and $B = 7.11 \times 10^8$ cm⁻⁴ produces well the actual dispersion of the LO phonon in the etching layer of the sample B. The fitted curve of the LO band using (1) and (2) is shown in dashed line in Fig. 2, which is consistent with the experimental curve. And the corresponding fitted result of the size (L) of GaAs nanocrystal particle is about 6.1 nm. Moreover, an AFM image of the GaAs granular

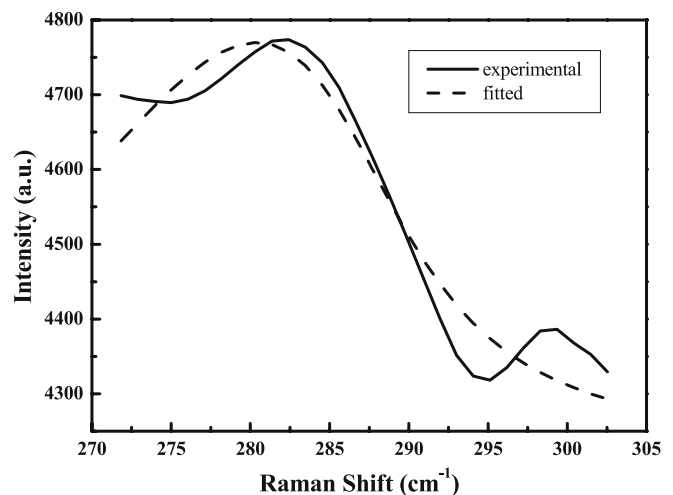


FIGURE 2 The LO band in the Raman spectrum of sample B prepared by a potential of 7 V in 0.1 M HCl at 50 °C and the theoretical fitted curve with the “spatial correlation” model

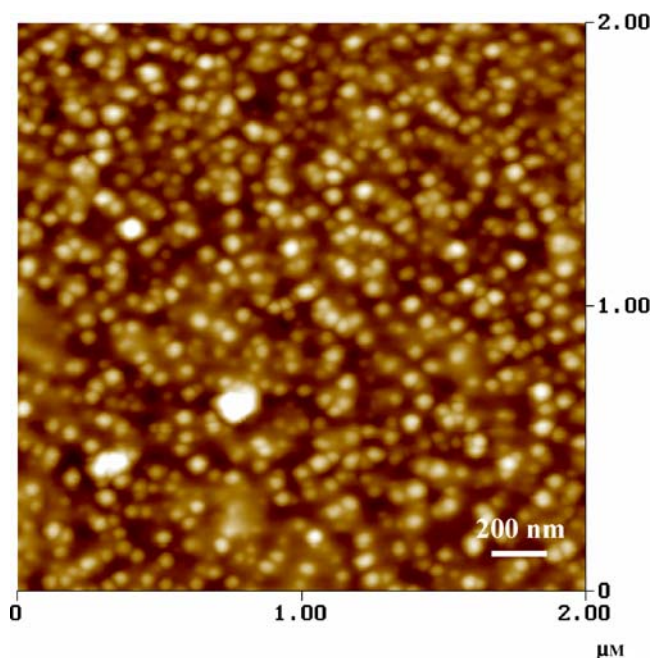


FIGURE 3 AFM image of the etched surface of sample B

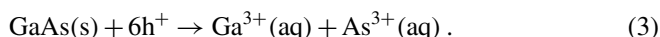
films has been obtained to confirm the existence of the nano-sized GaAs particles in the etching layer, as shown in Fig. 3. Most of the particles on the sample surface have a diameter in the range of 15–40 nm which is larger than the predicted size of GaAs nanocrystal by the “spatial correlation” model. This may be caused by the agglomeration of several GaAs nanocrystal clusters or the mixing of GaAs nanocrystals and the oxides (Ga_2O_3 and As_2O_3 will be discussed later).

The redshift, broadening, and asymmetry of the Raman peaks can also be explained by the phonon confinement model [25]. Above results show that the size of the GaAs nanocrystals in sample B is smaller than the exciton Bohr diameter (19 nm). So the phonons suffer spatial confinement leading to decline in uncertainty in position. As a result, the uncertainty in its momentum goes up, relaxing the $q = 0$ selection rule. Now, the off Brillouin zone center phonons become active and appear towards the lower energy tail. The full spectrum is the result of superposition of all these off center phonons, which results in the redshift, broadening and asymmetry of the Raman peaks.

As we have mentioned, some obviously new Raman peaks at 144, 167, 201, 417, and 475 cm^{-1} were observed for the sample B. It's reported that the As_2O_3 Raman spectrum at room temperature is very strong with the most intense peaks at 85, 183, 268, 369, 414, 471, 560, and 781 cm^{-1} , while Ga_2O_3 has a relatively weaker spectrum with the most distinct peaks at 201, 418, and 769 cm^{-1} [16]. Comparing these parameters with the Raman spectrum of sample B, most of the new Raman peaks are attributed to As_2O_3 and peaks at 201, 417 cm^{-1} are associated with Ga_2O_3 . This indicates the oxides (Ga_2O_3 , As_2O_3) have been formed in the etching layer of sample B during electrochemical etching process. To further confirm the chemical composition in the etching layer of sample B, an energy dispersive X-ray (EDX) measurement is carried out. It is found that the etching layer consists of O, Ga and As. The atomic amount composition is 7.8% O, 53.6% Ga and

38.6% As. This result further supports our deduction about the formation of oxides (Ga_2O_3 , As_2O_3) in the etching layer of sample B.

In order to make clear the process of oxidization during the anodic etching process, we used cyclic voltammetry (CV) in our discussion. The CV of the *n*-GaAs was carried out in 0.1 M HCl under electrolyte temperature of 50 °C and a rate of 50 mV/s. Figure 4 shows the polarization curve. The current density is less than 0.01 A/cm² when the anodic potential is smaller than 1.2 V, which could result from the formation of a blocking space charge layer (Schottky barrier) at the semiconductor/electrolyte interface by considering an *n*-type semiconductor/electrolyte junction under anodic bias [15]. After the turning point where the anodic potential is about 1.2 V, the current density has a distinct increase from 0.01 A/cm² to nearly 0.8 A/cm² until the anodic potential is about 4.7 V. This indicates the occurrence of the avalanche breakdown of the Schottky barrier and tunneling breakdown by considering the doping concentration at the turning point, and the surface of GaAs is dissolved by the following equation:



The Ga^{3+} , as well as the As^{3+} , is formed at the interface between electrolyte and solid phase, while the dispersed particles of Ga_2O_3 , As_2O_3 and GaAs appear in the solution [13]. With the anodic potential raising from 4.7 V to 8 V, the current density exhibits a relatively steady range from 0.83 A/cm² to 0.78 A/cm², which shows the effective resistance of the etching layer becomes larger during this process. This could be attributed to the formation of oxides on the sample surface, which is consistent with the results of Raman spectra.

Figure 5 shows temperature dependence photoluminescence (PL) spectra of the samples (including untreated *n*-GaAs, sample A and C). The PL spectrum of sample B will be discussed in detail later. From Fig. 5, two obvious “in-

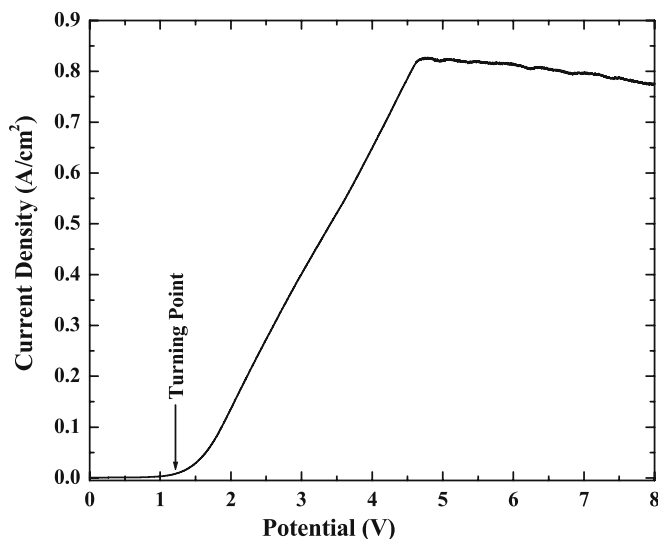


FIGURE 4 Polarization curves of *n*-GaAs (100) in 0.1 M HCl with a sweep rate of 50 mV/s

cm

Temperature

2x

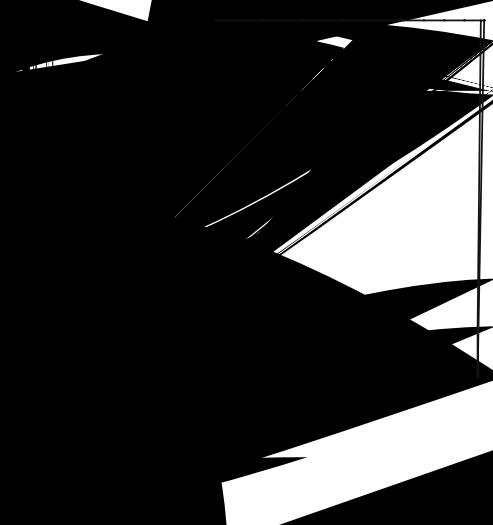
shown in Figure 1 can be found

peak intensity increases with the

intensity of the incident light

GaAs L band I is

the undoped GaAs



the surface of sample B during the anodic etching process. The PL peak of 540 nm and the PL peak of 475 nm have been observed for As₂O₃ [28] and Ga₂O₃ [29], respectively. So the I₄ PL band could be attributed to the photoluminescence of Ga₂O₃ and As₂O₃.

Above results show the “green” band envelopes in PL spectrum for the sample B could result from both the quantum confinement effect in GaAs nanocrystals and the photoluminescence of Ga₂O₃ and As₂O₃. While it is noticed that obviously new Raman peaks and the broad “green” band envelope have not been observed for anodic etched GaAs under higher etching temperatures (i.e., Raman spectrum of the sample C in Fig. 1 and PL spectra of the sample C in Fig. 5), which could be associated with either the brushing off of the oxides layer due to drastic reaction or the electropolishing on the sample surface during the etching process. These indicate that the microstructure changes of anodic etched GaAs under different etching temperatures result in the differences of their optical properties.

4 Conclusion

We have explored the microstructure and optical properties of the anodic etching layers of *n*-GaAs prepared at different etching temperatures. The Raman study reveals that the formation of GaAs nanocrystals and the oxides (Ga₂O₃, As₂O₃) on the etching layer is associated with the etching temperature, which is further confirmed by the AFM image and EDX analyses. The intensity of the two “infrared” PL bands I₁ and I₂ of the electrochemical etched *n*-GaAs is markedly stronger than that of untreated *n*-GaAs, while both the “infrared” PL bands do not reveal the systematic correlation with the etching temperatures. What is more interesting, for the sample prepared at etching temperature of 50 °C the broad “green” band envelope is stronger than any other samples, which is attributed to two factors: quantum confinement effect in GaAs nanocrystals and the photoluminescence of Ga₂O₃ and As₂O₃.

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