

Detection of excess crystalline As in GaAs: Native oxide overlayers by Raman scattering

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Abstract. Laser Raman spectroscopy was employed as a non-destructive probe for the detection and monitoring of crystalline arsenic in the native oxide films formed during heating of GaAs in air at various temperatures. Spectroscopy of oxide films formed after successive heating and etching treatments could confirm the location of arsenic to be near the top of the GaAs: native oxide overlayer.

Keywords. GaAs; native oxide; Raman scattering.

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1. Introduction

Native oxide films have been grown on GaAs by a variety of methods (Hasegawa and Hartnagel 1976; Chang and Sinha 1976; Murarka 1975; Berkovits *et al* 1988; Mizokawa *et al* 1978; Takagi *et al* 1978) including electrolysis, plasma anodization and furnace heating in various environments. To ascertain the quality of these films, for possible use in MOSFET devices, a variety of characterization methods are used and many of these methods involve removal of the oxide films. Since the performance of the oxide-gate devices is adversely affected by the presence of metallic arsenic, it is desirable to use a non-destructive method for detecting and monitoring of metallic arsenic in the oxide films during and after their growth. Laser Raman spectroscopy of oxide layers is one such method which works well due to the large Raman cross-sections of metallic arsenic contaminants, and is used in this work to follow the oxide film formation and etching of these films.

2. Experimental

The native oxides were formed on the $\langle 100 \rangle$ surface of GaAs samples during furnace heating in air for furnace temperatures in the range 350°C to 600°C and for heating times varying from a few minutes to a few hours. The semi-insulating GaAs samples, with polished $\langle 100 \rangle$ surfaces, were placed in a quartz boat and introduced into a single zone furnace. The oxidation was done in air and temperature was controlled

to within $\pm 5^\circ\text{C}$ and recorded by using a Pt–Pt.Rh. thermocouple attached to the boat. The Raman spectra of the heated samples were recorded in a backscattering geometry by using the 514.5 nm optical beam from an argon-ion laser in conjunction with a Ramanor HG-2S double monochromator, cooled Hamamatsu photomultiplier tube and photon counting electronics. We also used Raman spectroscopy to follow the gradual removal of the native oxide layers in successive chemical etching treatments.

3. Results and discussion

Figure 1(a–d) shows the characteristic Raman spectra exhibited by the pure GaAs $\langle 100 \rangle$ surface (figure 1a) and the thermally oxidized samples heated at different temperatures for 60 min (figures 1b–1d). The spectra in figure 1a shows a strong LO phonon line at 292 cm^{-1} which is allowed in backscattering geometry from the $\langle 100 \rangle$ face and a weak TO phonon line at 267 cm^{-1} which is not allowed in the scattering geometry but is often seen due to slight misalignment or small amount of disorder present at the surface. The spectra in figure 1b corresponds to the sample heated at 350°C for an hour and showed two important changes as compared to the reference spectra in the figure 1a. The peak height of the LO phonon line from GaAs decreased significantly indicating that the native oxide layer was formed at the surface and the layer significantly attenuated the incident laser light and the scattered Raman light from the GaAs substrate. In addition to this, a broad band was observed between 200 cm^{-1} and 250 cm^{-1} , which can be ascribed to amorphous arsenic (Lannin 1977; Schwartz *et al* 1979a, b). For heating treatments at temperatures greater than 350°C , two additional peaks, marked R_1 and R_2 in figures 1c and 1d, were seen in the spectra and these may be assigned to crystalline arsenic. These peaks were reported earlier by many investigators (Schwartz *et al* 1979a, b; Lannin *et al* 1975; Zitter 1971) and are discussed later in this paper.

Figure 2(a–e) shows the reference spectra from unoxidized GaAs surface (figure 2a) and the thermally oxidized samples heated in air for different times with a fixed heating temperature of 450°C . A broad spectral band appears between 200 cm^{-1} and 250 cm^{-1} in about 15 min of heating (not shown in the figure) and develops into a spectral line in about 30 min of heating, marked R_1 in figure 2b. Heating the samples for longer times (figures 2c–2e) results in a monotonic increase of the intensity of R_1 and R_2 lines, ascribed to crystalline arsenic as discussed later. An important feature of the spectra shown in figure 2 was the monotonic decrease of the LO phonon (292 cm^{-1}) peak intensity from the GaAs substrate which was interpreted as due to the increase in the thickness of the native oxide layer with increased time of heat treatment in air.

The results of isochronal heat treatments and isothermal heat treatments, shown in figures 1 and 2 respectively, give important information about the growth of native oxide films and the arsenic distribution in these films. In order to augment and further confirm this information, we recorded Raman spectra from the oxidized samples after successive etching treatments. In one investigation of this type, we used the oxide film formed by a one hour heat treatment at 450°C . The Raman spectra obtained after different etching times in a 1:1 $\text{H}_2\text{O}:\text{HCl}$ solvent are shown in figure 3. Figure 3a shows the spectra from the unetched starting sample. It shows the LO phonon from

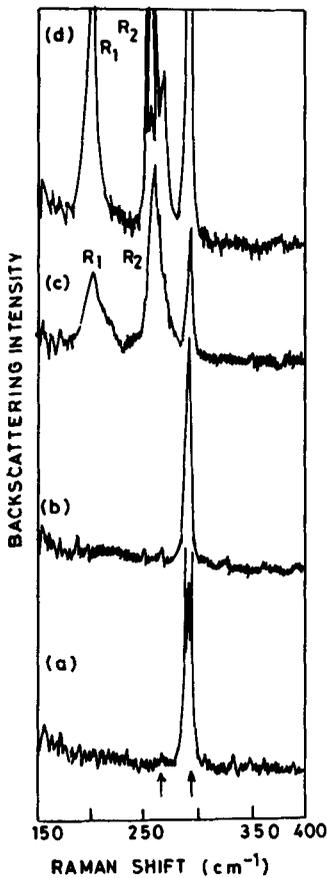


Figure 1. The Raman back scattering spectra from the $\langle 100 \rangle$ surface of pure GaAs (a) and the thermally oxidized GaAs samples heated for 60 min at 350°C (b), 450°C (c), and 600°C (d).

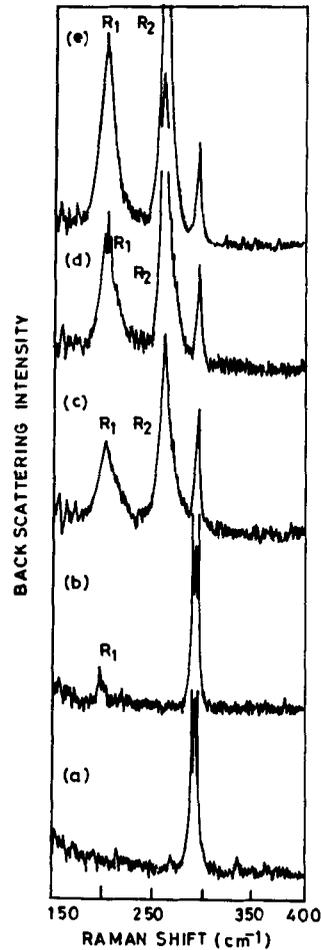


Figure 2. Back scattering Raman spectra from an unoxidized GaAs sample (a) and from thermally oxidized GaAs samples heated at 450°C in air for 30 min (b), 60 min (c), 90 min (d), and 120 min (e).

GaAs substrate and the R_1 , R_2 lines from crystalline arsenic. An etching treatment of about 150 min in HCl results in the removal of R_1 and R_2 lines as shown in the spectra of figure 3c. It is important to notice that the intensity of the LO phonon peak keeps on increasing in successive etching treatments of 180 min and 360 min shown in figures 3d and 3e. This indicates that the metallic arsenic layer is close to the interface between the oxide layer and the air. The intensity in the spectral line at 267 cm^{-1} , in figure 3c, may be indicative of disorder near the interface between the oxide layer and the GaAs substrate. The native oxide films formed by heating for an hour in air at 450°C could be fully removed using the 1:1 $\text{H}_2\text{O}:\text{HCl}$ solution for etching. In oxide films grown at higher annealing temperatures, say at 600°C for 30 min, we found that the same etchant could not fully remove the oxide films and it was necessary to use 50:1 (volume); methanol: H_3PO_4 solution to remove the oxides completely (figure 4).

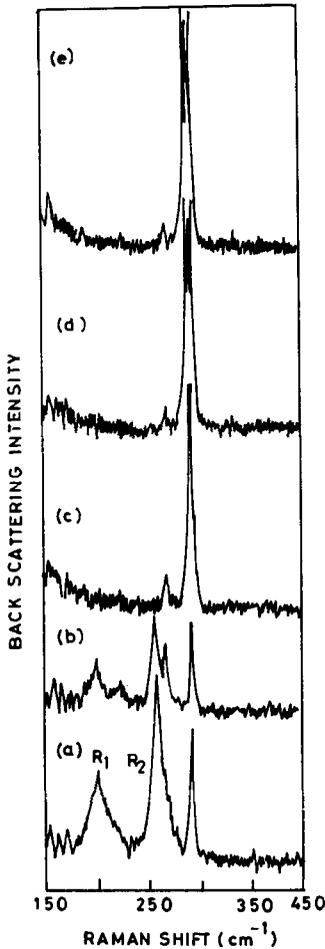


Figure 3. Raman spectra from a GaAs sample heated at 450°C for one hour (a). Spectra from the same sample etched in a 1:1 H₂O:HCl solvent for 120 min (b), 150 min (c), 180 min (d), and 360 min (e).

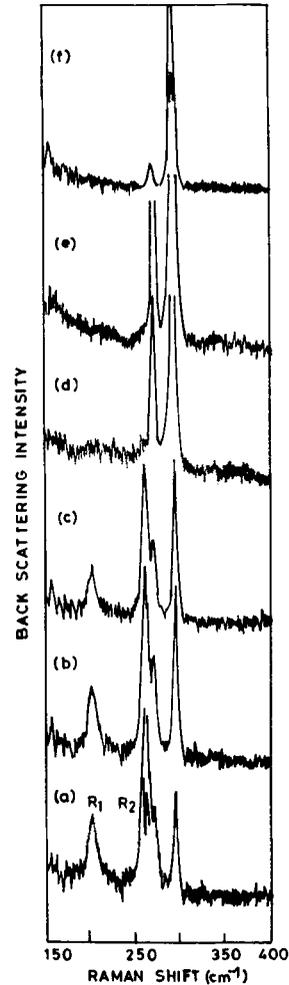


Figure 4. Raman spectra from the GaAs sample heated at 600°C for 30 min (a) and from the same sample subsequently etched in 1:1 HCl:H₂O solvent for 120 min (b) and 280 min (c). Raman spectra from the same sample further etched in CH₃OH:H₃PO₄ solution for 60 min (d), 120 min (e), and 180 min (f).

The origin of the two additional peaks, designated R_1 and R_2 in figures 1, 2 and 3 needs to be discussed briefly. The most significant features of these two Raman modes are that (1) their strength is comparable to the strength of bulk phonon lines of GaAs and (2) they are sufficiently narrow indicating well defined energies. The results presented by Cape (Cape *et al* 1977) on the basis of their Raman and X-ray photoelectron spectroscopic studies suggest that these lines may arise from an interfacial layer between the easily removed oxide and the substrate GaAs. This suggestion is in agreement with the speculations of Zaininger and Revesz (Zaininger and Revesz 1964) who proposed that thermal oxides and GaAs might have a composite structure with an arsenic rich interface region. This possibility has also been discussed

by Schwartz (Schwartz 1975). The observed intensities of these two R_1 and R_2 spectral lines and their line shapes rule out the possibility of their being the second order Raman spectra from the acoustic modes of GaAs (15). Farrow *et al* (Farrow *et al* 1977) concluded from the data collected by them that the frequencies of R_1 and R_2 peaks are dependent on the group V element of the III–V semiconductors and rule out the possibility that R_1 and R_2 peaks are due to Ga_2O_3 . The Raman spectrum from elemental arsenic is well known (Zitter 1971). The frequencies of R_1 and R_2 peaks (200 and 257 cm^{-1}) from the oxidized GaAs samples are almost the same as those for the double degenerate E_{ij} mode (195 cm^{-1}) and the A_{ig} mode (257 cm^{-1}) of the crystalline As. This interpretation agrees with our assignment of R_1 and R_2 peaks to a elemental arsenic layer.

Raman spectroscopy of native oxide films, formed on GaAs during isochronal and isothermal heating treatments in air, is used in this paper, in conjunction with the spectra of the same oxide films after successive etching treatments, to obtain a variety of information about the native oxide film formation. Qualitative information concerning the thickness of the oxide films could be obtained from the intensity of the LO phonon Raman line from the GaAs substrate since the intensity decreases as the film thickness increases. The signal at the LO phonon line (292 cm^{-1}) qualitatively monitors the film thickness during oxidation and etching treatments of the oxide films. The R_1 and R_2 lines are clearly related to a crystalline metallic arsenic layer close to the interface between the oxide film and air. The presence of crystalline arsenic could be confirmed for oxide films formed by heating at temperatures between 350°C and 600°C . The nature of the oxide films, however, is different for different temperatures used as is indicated from the different etching behaviours of films grown at different temperatures.

4. Conclusion

In conclusion, Raman spectroscopy provides a nondestructive technique for the detection and monitoring of metallic arsenic contaminants in the native oxide films formed by heating GaAs in air. We are investigating the possibility of using this technique for the evaluation of oxide films on GaAs formed by anodic oxidation and other methods.

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