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Photoluminescence study of GaAs homoepitaxial structures with different *in situ* substrate surface cleaning processes

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We have studied the substrate-film interface of GaAs homoepitaxial structures prepared by molecular beam epitaxy, employing three different *in situ* treatments for the substrate surface preparation: 1) Cleaning by hydrogen radicals (H*), 2) Exposure to trisdimethylaminoarsine (TDMAAs), and 3) The usual thermal cleaning under an arsenic flux. The concentrations of interfacial residual impurities of C and O were measured by secondary ion mass spectroscopy (SIMS). For semi-insulating substrates, the usual thermal cleaning process resulted in very high concentrations of C (2×10^{19} atoms/cm^3) and O (1.3×10^{18} atoms/cm^3) at the interface. The impurities were drastically diminished to below the SIMS detection limit by using the H*. We observed higher concentrations of impurities on Si-doped substrates. Photoluminescence results showed a clear correlation between the amount of interfacial impurities and signal intensity, the lowest the impurity content the strongest the photoluminescence intensity. The signal associated with the carbon impurity dominates the photoluminescence spectrum for homoepitaxial films in samples grown on semi-insulating substrates, while for samples grown on n^+ substrates the signal coming from the substrate dominates.

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I. INTRODUCTION

Substrate surface preparation is a very important issue in the production of high quality epitaxial films. In particular, it is known that the GaAs substrate surface prepared by the conventional thermal cleaning procedure under an arsenic flux prior to molecular beam epitaxial (MBE) growth, has high concentrations of residual impurities which yield to problems like the formation of a large carrier depletion region, resulting in a high resistance to carrier transport across the substrate-epilayer interface, and non-radiative trapping centers[1-3]. Moreover, in the fabrication of low dimensional structures, in which several steps involving lithographic processing and epitaxial regrowth are necessaries, the amount of interfacial impurities is a key factor influencing their quality[4]. Carbon and oxygen are impurities commonly found at the GaAs substrate-epilayer interface, therefore *in-situ* cleaning processes that effectively reduce these interfacial impurities are essential for the fabrication of high performance devices.

II. EXPERIMENTAL DETAILS

We present results of the characterization of GaAs epilayers grown by MBE on GaAs substrates in which different *in situ* substrate surface cleaning procedures were employed. First, the substrates were *ex situ* chemically

etched in a H_2SO_4:H_2O_2:H_2O (4:1:1) solution for 30s at 70 C, and mounted on molybdenum blocks using indium solder. Then they were introduced into the MBE system. We used three different methods of *in situ* substrate surface preparation: 1) Cleaning by hydrogen radicals (H*), 2) Exposure to trisdimethylaminoarsine (TDMAAs) which is a reactive gas that slightly etch the substrate surface, and 3) The usual thermal annealing under an As_4 flux. The amount of interfacial C and O impurities were determined employing secondary ion mass spectroscopy (SIMS). The samples were subject to optical characterization by photoluminescence spectroscopy (PL).

The MBE chamber used in the present work is equipped with gas cells for supplying organic sources (TMGa and TDMAAs) as well as effusion cells for evaporating metallic sources (Ga, Al, and As)[5]. TDMAAs was introduced through a gas cracker. The hydrogen radicals were generated by introducing H_2 through a W-filament cell heated at 1600 °C. In order to study the dependence of the interfacial impurity concentration on the substrate type, we used undoped semi-insulating (S.I.) and Si-doped n^+-type ($>1x10^{18}$ cm^{-3}) GaAs(001). Table I summarizes the cleaning procedures used for the samples

studied in this work. After the substrate surface cleaning, a 200 nm-thick undoped GaAs layer was grown by MBE at a substrate temperature of 580 °C. PL measurements were carried out at 18 K employing a standard set up with a He-Ne (632.8 nm) laser as excitation source.

III. RESULTS AND DISCUSSION

Figure 1 shows SIMS profiles for the samples grown on semi-insulating substrates. Notice the dramatic changes in the interfacial impurity content depending on the surface cleaning procedure. Figure 1(a) corresponds to the cleaning procedure commonly employed in MBE, annealing under an As_4 over-pressure at a substrate temperature of 570 °C. This usual thermal cleaning process resulted in very high concentrations of C (2×10^{19} atoms/cm^3) and O (1.3×10^{18} atoms/cm^3) at the interface. As observed in Fig. 1(b), the exposure to TDMAAs at a substrate temperature of 370 °C reduced the C concentration at the interface by more than two orders of magnitude, while the O concentration was reduced to a level near to the detection limit of the SIMS system. On the other hand, the use of hydrogen radicals at a substrate temperature of 570 °C, as shown in Fig. 1(c), allowed us to obtain a very drastic reduction in the amount of impurities to below the SIMS detection. Figure 1(d) shows the effect of using a lower substrate temperature with hydrogen radicals. So, it is clear that the substrate temperature plays an important role in the preparation of the substrates. It seems necessary to employ a temperature of about 570 °C when hydrogen radicals are used to obtain a reduced amount of interfacial impurities on SI-substrates. By employing hydrogen radicals at 370 °C the impurities content is reduced as compared with the traditional approach, however this did not gave us the best results.

The SIMS results obtained for samples grown on n$^+$-GaAs substrates are shown in Fig. 2. In general we observed that higher substrate temperatures are required to desorbe the GaAs oxide and clean this kind of substrates, this could be due to the formation of a thicker oxide on Si-doped GaAs substrates.[5,6] For this type of substrates the usual thermal cleaning process at a substrate temperature of 620 °C (Fig. 2(a)) resulted in a higher concentration of C at the interface than that obtained for S.I. substrates. For this type of substrate the cleaning with hydrogen radicals decreased the amount of interfacial impurities, but as shown in Fig. 2 (c) and (d), better results are obtained for higher substrate temperatures. As observed in Fig. 2 (b) the best results for n$^+$-GaAs substrates were obtained by exposing to TDMAAs at a substrate temperature of 420 °C. Table I summarizes the peak height values for the SIMS spectra presented in Figs. 1 and 2.

The generation of interfacial electric fields because of accumulation of impurities at the substrate-epilayer interface will have a strong influence on the transport of carriers. An evaluation of the interfacial electric fields was carried out and it was found a clear correlation between the electric field strength and impurity content. Samples with the higher amounts of interfacial impurities presented the strongest electric fields.[7]

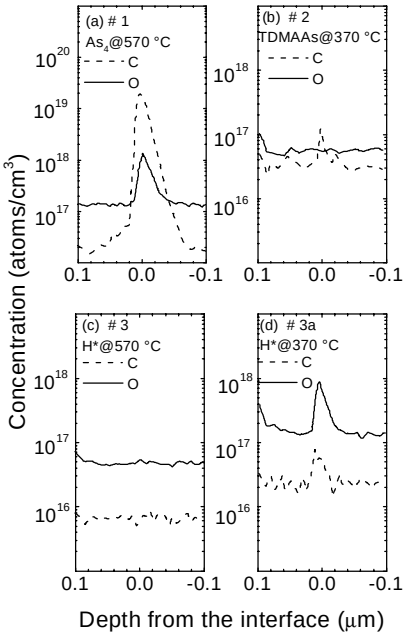

Fig. 1. SIMS depth profiles of C and O for samples grown on semi-insulating GaAs substrates.

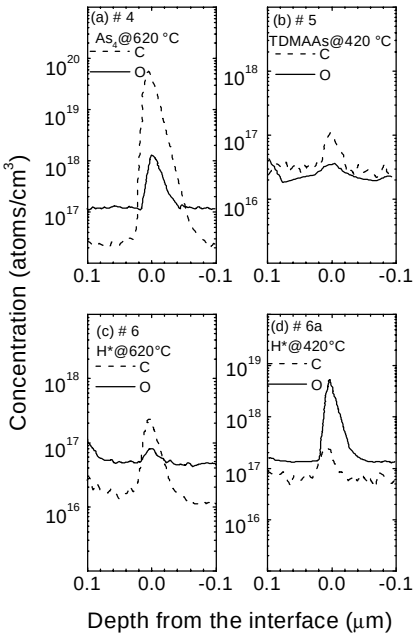

Fig. 2. SIMS depth profiles of C and O for samples grown on Si-doped n+-GaAs substrates.

TABLE I. Cleaning procedures for the studied samples. C and O peak heights at the interface were obtained from SIMS measurements.

Sample	Substrate type	Cleaning procedure	Cleaning time	C peak height (atoms/cm^3)	O peak height (atoms/cm^3)
#1	S.I.	As_4 at 570 °C	30 min	2×10^{19}	1.3×10^{18}
#2	S.I.	TDMAAs at 370 °C	30 min	1.3×10^{17}	a)
#3	S.I.	H* at 570 °C	100 min	a)	a)
#3a	S.I.	H* at 370 °C	100 min	7.5 x 10^{16}	9.0 x 10^{17}
#4	n^+	As_4 at 620 °C	30 min	6×10^{19}	1.5×10^{18}
#5	n^+	TDMAAs at 420 °C	30 min	1.3×10^{17}	a)
#6	n^+	H* at 620 °C	100 min	2.5×10^{17}	8×10^{16}
#6a	n^+	H* at 420 °C	100 min	2.5×10^{17}	5.5×10^{18}

a) Below the SIMS detection limit

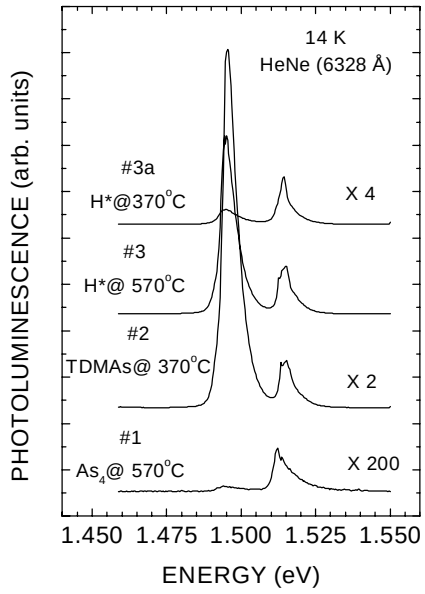

Fig. 3. Low temperature photoluminescence spectra of GaAs homoepitaxial films grown on semi-insulating GaAs substrates.

Even when impurities are localized near the interface film-substrate they affect the optical properties of the film. The presence of impurities increases the non-radiative recombination centers in which carriers are trapped. For optoelectronic devices is necessary to reduce as much as possible the presence of such centers. Photoluminescence spectroscopy affords a straightforward way to obtain information about the presence of non-radiative recombination centers. Figure 3 presents photoluminescence spectra for samples grown on semi-insulating substrates. The penetration depth of the 632.8 nm wavelength from the HeNe laser is around 230 nm for GaAs.[8] Thus, we are sensing the complete homoepitaxial film and part of the substrate. The overall features are the same in all the spectra and are characteristics of GaAs carbon doped films. There are two well defined regions with peaks around 1.495 eV and 1.514 eV, the lower energy peak has been ascribed to transitions from the conduction band to the acceptor carbon level.[9] In the structure at higher energy there are contributions from: free exciton (X), neutral donor-bound exciton (D^o,X), ionized donor-bound exciton (D^+,X), and the neutral acceptor-bound exciton (A^o,X) recombinations.[10] However, for the purpose of this work we will focus on the strength of the PL signal. For each cleaning procedure the PL strength constitutes a clear measurement of the effectiveness to obtain a material with excellent optical properties. In Fig. 3, the PL spectrum for the sample #1 prepared with the standard cleaning procedure, is about 200 times less intense than that corresponding to sample #3. Therefore PL spectroscopy permitted us to say that the GaAs film grown on a SI-substrate cleaned employing H* radicals at 570 °C is the best epilayer, in agreement with the SIMS results.

Figure 4 presents the PL spectra for the GaAs films grown on n^+-GaAs. As observed in this figure the spectra are very broad, and typical of a n^+-GaAs substrate.[11] Note that the homoepitaxial film may be considered predominantly as a p-type layer, then for these samples we have p-n junctions, where the interfacial electric fields could easily drive the photogenerated carriers towards the n^+-GaAs substrate. This could explain the substrate-dominated PL characteristics. The signal associated with

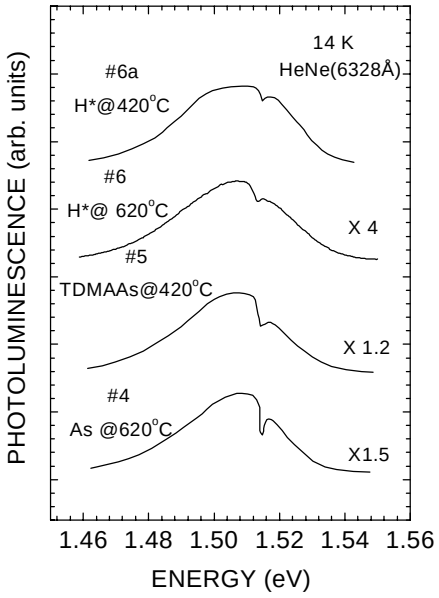

Fig. 4. Low temperature photoluminescence spectra of GaAs homoepitaxial films grown on Si doped n+-GaAs substrates.

the homoepitaxial film is around 1.518 eV, which could be associated to transitions between bound excitons to carbon acceptors. For these samples there is not a clear trend between PL intensity and impurity content. It is worth to mention that atomic force microscope images showed that the substrate surfaces after the cleaning procedures are substantially rougher than those corresponding to the SI-substrates. The above mentioned substrate characteristics along with the stronger interfacial field for these samples could explain the strengths observed in the PL spectra for GaAs layers grown on n^+-GaAs substrates.

IV. CONCLUSIONS.

In summary, a clear correlation between the PL strength and the interfacial concentration of C and O was observed for SI-substrates. For these substrates, the usual thermal cleaning process resulted in very high concentrations of C and O at the interface, producing a large electric field and a very low PL intensity. The impurities were drastically diminished to below the SIMS detection limit by using the H*-cleaning, and as a result the PL intensity increased up to 200 times as compared with that obtained by the standard cleaning procedure. On the other hand, for the Si-doped substrates, we systematically observed higher concentrations of impurities, and the PL spectra were dominated by the n^+-substrate signal. According to SIMS measurements on this type of substrates the best results were obtained by exposure to TDMAAs.

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