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Soft laser sputtering of GaAs semiconductor surfaces

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1. INTRODUCTION

Laser sputtering of III-V compound semiconductors is currently the subject of experimental and theoretical investigations for potential applications in optoelectronics (processing or improvement of devices, production of original surface structures). Elemental analysis of doping or impurity concentrations in GaAs/GaAlAs multilayer structures with depth resolution of a few nanometers, which also minimises mixing at the interfaces is an important challenge. For this purpose, sputtering with low fluence UV laser is regarded as an interesting alternative to the conventional ion beam sputtering method.

We have studied the soft laser sputtering of GaAs surfaces with 337 nm photons, starting from the threshold for particle emission (a few tens mJ/cm²) up to 220 mJ/cm² fluences. Particles (atoms and molecules) sputtered from the irradiated surface are detected, their relative number measured and their time-of-flight determined using laser resonant ionisation mass spectrometry (RIMS). The surface state after laser irradiation is examined by SEM and X analysis.

2 - EXPERIMENTAL STUDY

The experimental set-up described in details in Ref.1 is mainly composed of an ultra-high vacuum chamber equipped with a sample manipulator and a quadrupole mass-spectrometer. The GaAs sample is irradiated by the beam of a N₂ laser (337 nm) of 10 ns pulse duration and 10 Hz repetition rate. After aperturing and focusing on the sample with an $f = 30$ cm lens at a 60° incidence angle, the maximum fluence is about 220 mJ/cm². Atomic and molecular sputtered species are detected by the mass-spectrometer, directly in the case of ionized particles and after resonant multiphoton ionization by the second harmonic of a tunable Nd: Yag pumped dye laser for the neutrals. This probe laser pulse is fixed with an adjustable delay (0 to 14 μ s) with respect to the N₂ laser pulse.

2.1 Photoionization spectrum of Ga and As species

Ga° atoms are probed in their $^2P_{1/2}^o$ ground state by (1+1) resonant multiphoton ionization at $\lambda = 287.5$ nm, whereas ionization of As° atoms requires a (2+1) multiphoton process at $\lambda = 286$ nm ($^4S_{3/2}^o \rightarrow ^4D_{1/2,3/2}$ 2-photon resonances). In fact, scanning the probe laser wavelength around these two resonances, we observe the spectrum shown in Fig.1. It is composed of three lines, the unexpected broader line being attributed to a (1+1) photon transition at $\lambda = 286.127$ nm starting from the $^2P_{3/2}^o$ excited state (18186 cm⁻¹). It will be shown in the following that this spectrum results from the photodissociation of As₂ molecules which constitute the largest part of the sputtered arsenic species. According to this result, the photoionization schemes leading to the observed spectrum are :

A part of As_2 molecules are also photoionized without dissociation by three-photon absorption. The spectrum is relatively flat in the 287 - 290 nm range. On the contrary, the Ga_2 photoionization spectrum presents structures characteristic of rovibrational bands.

Fig. 1- Photoionisation spectrum of laser-sputtered arsenic

2.2 Time of flight distributions

Time of flight (TOF) distributions of Ga^o , As^o and As_2^o species were measured by delaying the probe laser pulses with respect to the N_2 laser shots. The results shown in Fig. 2 correspond to 170 mJ/cm² N_2 laser fluence and a probing distance of 3.6 mm above the sample surface. One observes that As^o and As_2^o species have the same TOF. This proves that the observed As^o photoions originate mainly from the photodissociation of As_2^o molecules, i.e. arsenic is mainly sputtered by laser irradiation in the form of diatomic species and not as atoms, contrary to gallium.

The TOF distributions of Ga^o atoms and $(As^o)As_2^o$ molecules are well fitted by half-space Maxwellian distributions characterized by kinetic temperatures.¹ They are in broad agreement with the results obtained from a model of laser heating of the surface. In the conditions of soft laser sputtering, the energy of the sputtered particles reflects the "thermal" state of the surface. The particles temperature as well as the surface temperature increase with the laser fluence, reaching the melting temperature of GaAs (1500 K) for 200 mJ/cm².

Fig. 2 - TOF distribution of Ga and As species
Fit by Maxwellian functions with $T = 1350K$

2.3 Laser Sputtering Yields

a- shot number dependencies

The variation of the sputtering yield with the number of laser shots on the same spot is shown in Fig. 3 for Ga^o and $(As^o)As_2^o$ for different laser energies. During the first laser shots, one observes a very large emission of particles, followed by a fast decrease. After one thousand laser shots, the signal is decreased by a factor of 2 for Ga^o and up to 10 for $(As^o)As_2^o$. Then, the yields decrease slowly and tend towards a quasi stationary regime for a number of shots greater than 10^4 . This behaviour is roughly observed whatever the laser fluence is. However, one must distinguished two fluence ranges.

For low laser values (from the threshold to 85 mJ/cm²), As emission vanishes after a few thousand laser shots. This can be interpreted as the sputtering of the surface defects resulting from localized absorption on the defect sites followed by bond breaking.² It must

be noted that in this low fluence range, the kinetic temperature of the sputtered particles as well as the calculated surface temperature are less than 800K, that is much lower than the melting temperature of GaAs (1500K) and the critical temperature for strong As_2 vaporisation (950 K).³ In the medium fluence range (85 - 220 mJ/cm^2), the sputtering yields tend towards a near constant value after a large number of shots. However, a fine examination of the Ga/As sputtering yield ratio shows that the composition of the irradiated zone evolves as the shot number increases : the ratio increases due to the slow but continuous As-impooverishment of the irradiated surface.

Fig.3 - Laser sputtering yields of Ga and As as a function of the number of laser shots

This behaviour is correlated to the strong emission of As species in the form of As_2 molecules at the beginning of the sputtering. The preferential sputtering of arsenic leads to the formation of a perturbed Ga-rich structure after a few laser shots. This initial transformation seems to determine the further evolution of the irradiated surface in an irreversible way. Contrary to the case of InP where preferential sputtering of P was also observed,⁴ no compositional equilibrium of the altered surface is reached for GaAs. This is probably due to the particular thermodynamical properties of this material which incongruently evaporates for temperature larger than 950K. For example, at 1300K, the partial pressure of As_2 and As_4 is more than 2 orders of magnitude larger than for Ga. According to our TOF measurements and the calculations, this surface temperature should be obtained for only $\sim 170 \text{ mJ}/\text{cm}^2$ laser fluence.

2.4- Scanning electron microscopy and X analysis of the irradiated spots

The above discussion related to preferential sputtering of As_2 and the consecutive formation of a perturbed Ga-rich surface is illustrated by the microscopic analysis of the structural and compositional changes of the irradiated spots, for different numbers of laser shots. For example, Fig. 4 reproduces an image of the surface irradiated by 2×10^5 220 mJ/cm^2 laser shots. X analysis of the As and Ga contents are given for different positions in the perturbed zone. Different structures are observed in the form of droplets, flakes and piles. All these structures show a large reduction of the As concentration. One observes also that this reduction is the largest at the spot center, according to the laser energy distribution. But, the compositions of the spot center and droplets surrounding the spot are quite similar : the As/Ga ratio is reduced to 0.16.

The formation of Ga-rich droplets is also observed for low laser fluence (40 mJ/cm^2) but after $\sim 7 \cdot 10^4$ laser shots and for moderate fluence (125 mJ/cm^2) after only $2 \cdot 10^4$ shots. In Ref. 5, similar production of Ga clusters after 5 mm thermal annealing of a GaAs surface at 930 K was reported. By analogy, we might consider that the laser pulse acts as a pulsed heating source increasing the surface temperature. According to the particular phase

diagram of GaAs, when exceeding a critical value, this temperature increase leads to the preferential emission of arsenic in the form of molecules. This induces the formation of a Ga-rich surface structure. In the case of low laser fluence (i.e. below the critical temperature), the process could be initiated from the heating of surface defects which are weakly bound to the surface. In both cases, this initial transformation seems to determine the further evolution of the irradiated surface. Following As_2 emission, unbounded Ga atoms aggregates to form Ga islands on the surface. After a sufficient number of shots, micrometric structures are produced which finally behave as the pure Ga metal. This evolution of the surface state after multipulse laser irradiation appears to be practically the same for low and medium laser energies, the only difference being in the number of shots required to obtain the same microscopic structure.

Fig. 4 -SEM and X analyses of the irradiated zone. a) virgin surface, b) droplets, c) spot centre

3 - CONCLUSION

Despite the very unusual behaviour of laser sputtering of GaAs compared to InP^4 and GaP^2 , it appears that the interaction mechanisms are mostly thermal. The gross features of the experimental results can be interpreted from the particular thermodynamics properties of this compound which exhibits very large As_2 vapour pressure above the solid as soon as the temperature exceeds the critical value. After a few laser shots, corresponding to particle emission from defect sites, the thermodynamics of GaAs appears to govern the further evolution of the laser sputtered surface.

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