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INVESTIGATION OF BURRIED INTERFACE ($\text{Si}_3\text{N}_4/\text{Ga As}$) BY EXAFS IN TOTAL REFLECTION AND DISPERSIVE MODE

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Résumé :

Etudier l'interface sous un film de passivation est souvent impossible. La spectroscopie d'absorption X par réflectivité totale permet de réaliser une telle approche si le film déposé est de densité plus faible que le substrat. C'est le cas de Si_3N_4 sur Ga As. Les deux méthodes de préparation utilisées conduisent à des interfaces de structure différente. La méthode PECVD donne une interface homogène tandis que la méthode du plasma réactif produit également en faible quantité des liaisons GaN. Dans ce dernier cas un modèle d'îlots de GaN serait en accord avec l'étude XPS.

Abstract :

To reach a buried interface below the passivating film is often out of the capability of experimental technique. The X-ray absorption, spectroscopy using the total reflection scheme allows such investigation if the deposited film has a lower electronic density than the substrate one. This requirement is fulfilled with Si_3N_4 on Ga As. Two considered processes leads to interfaces with large differences. PECVD keeps well-defined reflecting surface, while the cathodic reactive sputtering gives rise to an island-type one, this results agree with XPS measurements.

Although plasma deposited silicon nitride is widely used to passivate or encapsulate Ga As (100) wafers, little is known about the interfacial chemistry between Ga As and the insulating layer. X-ray absorption spectroscopy using the total reflection scheme is suited to investigate the very first 25 Å of the semiconductor below the Si_3N_4 passive layer. This technique is able to penetrate the topmost surface layer and retrieves information from a buried interface provided the upper film is of low electronic density compared to the substrate. The energy dispersive spectrometer (1) presently used gives minor additional advantages mainly in term of data collection time. Each reported spectrum is an average of about 30 spectra each of them taken in 13.6 s.

Passive layer elaboration

Three samples were elaborated at the Thomson's Laboratory using 2inch-GaAs wafers. In addition we ground a small GaAs crystal to obtain standard measured in transmission mode. In the present paper we focus our attention on two different process of deposition : plasma enhanced chemical vapor deposition and reactive sputtering after a subsequent cleaning of the Ga-As wafers into acidic and basic solutions.

Sample =1 : Si_3N_4 is deposited in a Plasma Enhanced Chemical Vapor Deposition reactor (PECVD) . A cylindrical quartz reactor is placed in a three zone furnace. Vertical substrate holders made of graphite are placed in the temperature plateau and are connected to a 13.56 MHz generator. The decomposition of silane and nitrogen is controlled by the R.F. power. All the parameters

(temperature, gas flows, pressure) are computer-controlled. During the Si_3N_4 deposition the pressure was 0.75 torr, the temperature 350°C , the gas flows $12\text{ cm}^3\text{S}^{-1}$ and $1500\text{ cm}^3\text{S}^{-1}$ for silane and N_2 respectively. The R.F power was set at 6w. In these conditions the deposition rate is 25 Å/minute and the optical index is 2.1.

Sample =2 : The Si_3N_4 layer was deposited in the same conditions than sample =1. But before Si_3N_4 deposition the surface was exposed to a nitrogen plasma operated as 0.75 torr and 350°C also. The R.F power had been 10 W for 15 minutes in order to create a GaN layer. For both samples =1 and =2 the Si_3N_4 thickness was adjusted to 175Å.

Sample 3= : After relevant chemical cleaning and annealing treatment the nitride is deposited using cathodic reactive sputtering. The Si_3N_4 thickness was 200 Å.

DATA COLLECTION. The crucial point when the EXAFS signal is carried out by the totally reflected beam is to set the position of the sample accurately. Our device includes three encoded vertical translations. Two of them (10cm-separated) defines the rotation axis, the third one (20cm away along the beam path) allows to tune the glancing angle.

The 2inch-long Ga As wafers reflect a 100μ -thick beam slice when the glancing angle is set at 0.4 mrad. Hence, because of our beam vertical size a loss of intensity by a factor 20 is already achieved compared to the transmission scheme(2). It has been pointed out that optimized data are obtained when the sample orientation is adjusted to about 0.8-0.9 times the critical angle in order to reduce the contribution of the real part of the index to the EXAFS modulations (3). This residual effect does not affect the periodicity of the oscillations but conclusions drawn from the EXAFS amplitude would be irrelevant.

The dispersive configuration concentrates the beam onto a few mm-wide band of the sample but gives our experiment more sensitive to dust or particles on windows, or reflecting surface since it affects locally the beam path and its local intensity. This last point is a concern added by the reflected scheme. An other way to produce "glitches" arises from the perfect crystallinity of the substrate which generates Bragg reflections for specific energies.

Finally the dispersive scheme does not include an intrinsic calibration. The energy scale obtained in the preliminary transmission mode is useless. The surface is always slightly tilted which induces a shift of the energy-pixel number correlation. To overcome this inherent difficulty we always used the reflected beam as a primary beam in which we inserted the homogeneous thin GaAs standard sample.

A last but not least need is to know the hypothetical intensity versus photon energy given by a perfect non absorbing surface in order to calculate the absorption. A practical way to do that is to substitute a platinum-coated float glass to the GaAs sample. Hence the geometry remains unchanged and the I₀ profile can be derived. It is obvious that this technique requires mirror of very high quality.

RESULTS

XPS have been used to investigate these different samples (4). The thickness, of silicon nitride layers deposited on GaAs, has been limited to about 40 Å in view of the investigation of the interface GaAs-silicon nitride by XPS. GaN has been observed through chemical shift in Ga (LMM) AUGER line on two samples (CVD enhanced plasma preceded by N_2 plasma and reactive sputtering). The Auger chemical shift between GaAs and GaN has been found to be equal to 2.2 eV, in agreement with the value of HEDMAN et al (5). On the last sample, no GaN has been detected. The stoichiometry of the silicon nitride on the different samples, as judged by XPS, is the same within the experimental error of XPS. (fig.1). X-ray absorption data have been collected for both Ga and As K-edges. In the total reflection scheme different artefact (Bragg reflection, ..), signal/noise ratio may limit the significant data range.

Ga-K edge Fourier transforms has been calculated using a flat window between 30 eV and 190 eV ended by two cosine tails. In addition of the three F.T., the first curve of fig.2 shows the F.T. of the GaAs spectrum collected in the transmission mode.

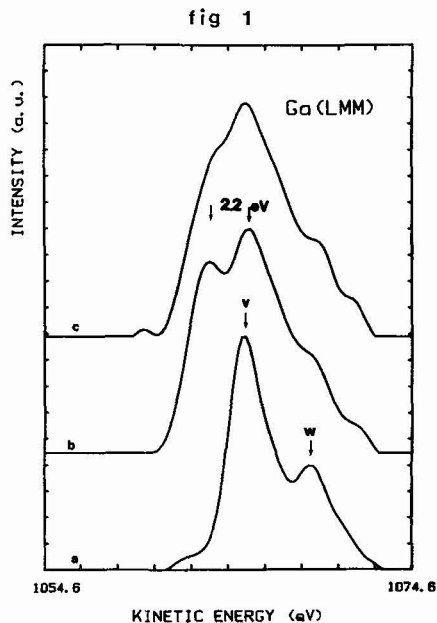


Fig. 1- XPS : GaLMM Auger peaks. The GaAs peak (v) has a shoulder (w) on the high energy side because of the spin-orbit coupling. Note the 2.2 eV chemical shift observed for sample =2(b) and the unresolved structure of sample =2 to sample =3.

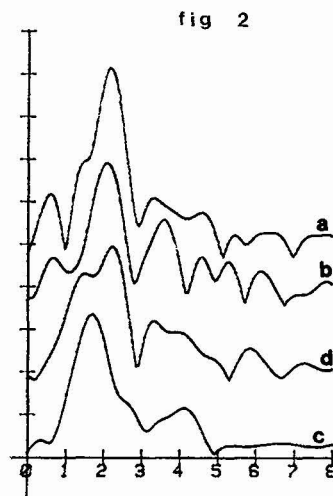


Fig. 2- Ga K-edge : K Fourier transforms
 a) GaAs in transmission mode
 b) sample =1 (PECVD). The FT peak is located at the GaAs position.
 c) sample =2 (PECVD + N_2 plasma).
 The FT peak position shows that the GaN sublayer is the reflecting surface.
 d) sample =3 (Reactive Sputtering).
 Both GaN and GaAs contribute to the FT first peak.

Sample =1 appears free of GaN as expected since the smooth deposition does not alter the Ga/As ratio as checked carefully by angle-resolved photo emission (4). The first peak points exactly at the GaAs bond length, uncorrected for the phase shifts. Sample 2=, on the contrary exhibits a peak of the F.T shifted to the lower R value which is assigned to GaN bond length. It may remain a small contribution of GaAs as shown by the shoulder on the high R side. For samples =2 and =3 with an intermediate sublayer the reflecting interface is the first one (Si_3N_4 -GaN) since its critical angle $\theta_c(\text{GaN})$ is almost equal (only 6% lower) to $\theta_c(\text{GaAs})$. Thus we are probing mostly GaN if this intermediate layer is thick enough (~ 20 -25 Å). Since the GaAs contribution in the F.T is almost cancelled one can infer that such thickness is achieved. This result is in contradiction with the XPS measurements (fig.1) performed with a similar but different sample since XPS requires a thin Si_3N_4 layer limited to 40 Å instead of 175 Å in our case. The X ray-excited Ga LMM Auger peaks is splitted because of the 2.2 eV chemical shift of the GaN bond with respect to the GaAs one. The intensities tell us that about 40% of Ga is bound to nitrogen. Because of the high energy of the Ga LLM Auger electron the probe depth is about 25 Å which is very similar to the depth of penetration of the evanescent wave in the total reflection scheme. XPS is more consistent with a 3,4 GaN monolayers which is half that one can infer from x-ray total reflection.

Sample =3 . The cathodic reactive sputtering (RS) process produces an interface where both GaN and GaAs bonds are mixed as shown by the splitted F.T. first peak (fig.3d). XPS shows the same feature. In addition angle-resolved XPS checks that the Ga/As ratio is relevant to a preferential erosion of As. This is not the case with PECVD (sample =1). At the opposite of PECVD, RS gives rise to a "rough" interface including GaN formation. The unresolved double structure shown by XPS (fig. 1) may be related to charge effects when GaN islands are disconnected.

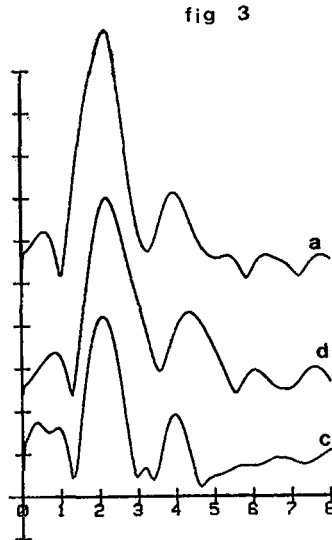


Fig. 3- As K-edge : k^3 Fourier transforms
 (a) AsGa in transmission mode
 (c) sample =2
 (d) sample =3 In both samples As atoms are linked
 to Ga atoms

As K-edge Data on sample =1 were not reliable for unknown reasons up to now. Thus we restrict fig. 3 to the three F.T. of the standard, sample =2 and =3. All F.Ts clearly show the lack of significant change from the Zinc-blende original environment. That is very consistent with XPS measurement. When a GaAs is broken, As atoms evaporate and are not trapped within the Si_3N_4 film.

CONCLUSION. Investigation of buried interface using the total reflection scheme allows to probe the very first 25 Å penetrated by the evanescent wave. This capability of a very shallow investigation is an advantage compared to fluorescence or total yield detections. The FTs differentiate the nature of the two processes of Si_3N_4 elaboration.

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