

Photons and Low Energy Particles in Surface Processing

Symposium held December 3-6, 1991, Boston, Massachusetts, U.S.A.

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SURFACE STUDIES OF LASER PROCESSING OF W ON GaAs FROM WF_6

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ABSTRACT

Laser Chemical Vapor Deposition of tungsten on GaAs from WF_6 using a focused cw scanning argon-ion laser beam has been investigated. Lines have been produced using different mixtures of $WF_6:H_2$ and $WF_6:SiH_4$ and in some cases, without any reducing gas. Depositions are found to occur within a narrow process window, and are difficult to reproduce. In order to understand this process, we have performed surface analysis on GaAs samples exposed to WF_6 . X-Ray Photoelectron Spectroscopy studies on the interaction between WF_6 and GaAs in the absence of laser illumination show that fluorinated tungsten compounds are present on the GaAs surface. Furthermore, the existence of a chemical reaction leading to the formation of GaF_3 at the surface and to a loss of the stoichiometry of the substrate surface is detected. Possible mechanisms, and the effects of these reactions on the deposition process are discussed.

INTRODUCTION

It has recently been reported (1,2) that W is a good material for forming Schottky contacts on GaAs, since W is a low resistivity refractive metal and does not react with Ga or As below 1000°C (2). As laser chemical vapor deposition (LCVD) is a selective and low temperature process, it is an attractive technique for depositing W on temperature sensitive substrates such as GaAs. We have previously presented preliminary results on LCVD of W from WF_6 on GaAs (3).

We present here the results of the LCVD of W on GaAs using a cw Ar⁺ laser. Lines are deposited in a narrow process window but are difficult to reproduce. In some cases, deposits are obtained without any reducing gas, suggesting that GaAs plays a role in the deposition. We then report on the interaction between WF_6 and GaAs under the conditions of laser deposition using X-ray Photoelectron Spectroscopy (XPS). We found that the surface oxides (especially As_2O_3) react with the WF_6 atmosphere, leading to a highly surface localized reaction. Tungsten subfluorides and oxyfluorides are chemisorbed onto the surface, where a loss in As and formation of GaF_3 are detected.

LASER PROCESSING OF W ON GaAs

The substrates are (100) semi-insulating liquid-encapsulated Czochralski GaAs. Samples are degreased in hot trichloroethane, acetone and propanol, rinsed in deionized water then etched in $H_3PO_4:H_2O_2:H_2O$ (1:1:10) for 5 seconds. Samples are then rinsed in hot $HCl:H_2O$ (1:1) for 5 minutes and then in deionized water and dried in flowing nitrogen.



The laser direct writing system has been described elsewhere (3). It consists of a 514 nm cw Ar⁺ laser focused on the substrate which is placed in a stainless steel chamber with a quartz window. This chamber is mounted onto computer controlled X-Y translation stages having a spatial resolution of 0.1 μ m and a maximum scan velocity of 100 μ m/sec. Once the sample is placed for processing, the chamber is pumped to a primary vacuum and heated to nearly 80°C with a 100scm Ar flow for more than an hour before WF₆ and the reducing gas are introduced. All experiments are done under static filling conditions.

Lines are deposited using a mixture of WF₆ and H₂ at a velocity of 25 μ m/s and using laser power between 57 and 75 mW. The most favorable conditions correspond to a partial pressure of 10 Torr of WF₆ for a 1.5 or 1:10 ratio of WF₆:H₂. The film thicknesses range from 10 to 80 nm and the growth rate is estimated to be close to 230 nm/sec. Auger Electron Spectroscopy (AES) depth profiles made on these lines show a substantial As incorporation through-out the deposit, which consists of less than 30% W (4). Deposits could also be obtained by using SiH₄ as a reducing gas, as suggested by Black et al. (5). However, we found that the results are very different from those obtained with other substrates (6) and are very difficult to reproduce. Success in obtaining deposits was found to vary even as we scanned different regions on the same sample(4). In some cases, W lines are even obtained without any reducing gas, with a WF₆ partial pressure of 10 Torr and scan speed of 25 μ m/s. These observations prompted us to investigate the basic interaction between WF₆ and GaAs in the conditions of laser deposition.

SURFACE ANALYSIS OF THE GAS-SUBSTRATE INTERACTION

For the XPS study of the gas-substrate interaction, the same cleaning and pre-deposition procedure as those employed for deposition are used, in order to reproduce the conditions of the LCVI experiments. All samples are surface analysed after cleaning, in order to provide a good knowledge of the initial surface condition, and then transferred in vacuum to an adjacent reaction chamber, using a transfer module. Once the substrate is exposed to WF₆, the chamber is then pumped to a primary vacuum and the sample is transferred back to the XPS spectrometer for analysis. All spectra are taken in a VG ESCALAB MkII spectrometer, using Al K α radiation (1486.6 eV) of the nonmonochromatized source. By using this ray, we are able to monitor the highly surface sensitive 2p lines of Ga and As (2), the mean photoelectron escape depth, (<1nm) as well as their bulk sensitive 3d lines (>2nm).

Figure 1 shows the 3d As peak both before and after exposure of a clean GaAs surface, to 10 Torr of WF₆ for 10 minutes. The small feature at around -37 eV after exposure is due to the W 4f core levels. Note that no metallic tungsten is detected, since the metallic peaks should be at energies close to -31 eV (the peak observed at this energy is simply the satellite peak of the As 3d). Since the shift of the W peak to higher binding energy is greater than 5 eV we conclude that the adsorbed W is still bonded to fluorine and possibly to oxygen. This adsorption is probably dissociative, as the ratio between the total W 4f and the F 1s (-684.9 eV) signals is close to 1:4. Moreover, we do not expect to detect any WF₆ adsorption because WF₆ is volatile at room temperature in a vacuum environment. The presence of a broad unresolved W 4f emission doublet suggests that the W on the surface is present in at least two differently coordinated compounds, WF_x and WO_xF_y.

The 3d As peak before exposure shows the presence of some As₂O₃ by the presence of a small peak, shifted by 3 eV from that of As bonded to Ga, at -41.2 eV. By comparing the oxide and substrate intensity for the 3d and the 2p_{3/2} peaks respectively, we estimate that a 7A oxide layer, consisting mainly of As₂O₃ and Ga₂O₃, is formed as the samples are exposed to air between cleaning and the start of

each experiment. Our angle resolved XPS studies on cleaned GaAs have shown that As₂O₃ is highly localized at the surface of the substrate. Therefore, if no As₂O₃ were lost after the WF₆ exposure, the corresponding peak should increase relative to the peak of As bonded to Ga, as we are then sampling a lesser depth of the substrate. Therefore, the decrease of the As₂O₃ after exposure to WF₆ suggests that WF₆ reacts with this oxide.

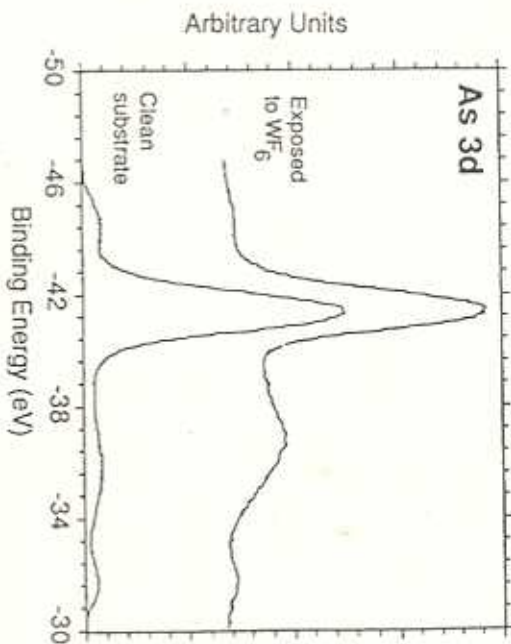


Figure 1. XPS spectra of the As 3d peak of clean GaAs before and after exposition to 10 Torr of WF₆ for 10 minutes.

In Figure 2, the Ga 2p_{3/2} peak presents a tail towards higher energies. After exposure to WF₆, it extends further that the 1.4 eV shift due to Ga₂O₃, detected on the peak of the clean sample. This could be accounted for by the presence of some Ga bonded to an element more electronegative than oxygen, such as fluorine. Indeed, this peak cannot be deconvoluted using only GaAs and Ga₂O₃ contributions and has been deconvoluted, assuming three contributions: the first is at -1117.2 eV for Ga in GaAs, the second is at -1118.6 eV for Ga₂O₃ (7) and the third is at -1119.4 eV and is attributed to GaF₃. This deconvolution presented in Figure 3. The presence of fluoride is less clearly detected on the bulk sensitive Ga 3d peak. If we calculate the total As/Ga ratio, we see that it is reduced to about 0.7 for the 2p_{3/2} peaks, while it stays practically constant for the 3d peaks. These observations indicate that this reaction takes place only near the surface. This is confirmed by angle resolved XPS studies on these samples.

Evidence that the peak at -1119.4 eV is indeed due to the presence of GaF₃ was obtained when we exposed a clean GaAs sample to 10 Torr of WF₆ and pumped the reaction chamber to base pressure, and then irradiated the sample by a perpendicularly incident KrF pulsed excimer laser beam. Since the average W-F bond energy is typically 2.8 eV, the 5 eV photons of the KrF laser beam might strip one fluorine atom from the WF_x or WF₆ adsorbed on the surface, leading possibly to the formation of metallic W. The W 4f_{7/2} peak having a binding energy of -31 eV shows that the W on the surface of the sample is indeed metallic, so that the fluorine detected is entirely bonded to Ga. The ratio between the F 1s peak (at -685.7 eV) and the GaF₃ contribution to the 2p_{3/2} Ga peak is indeed close to 3.

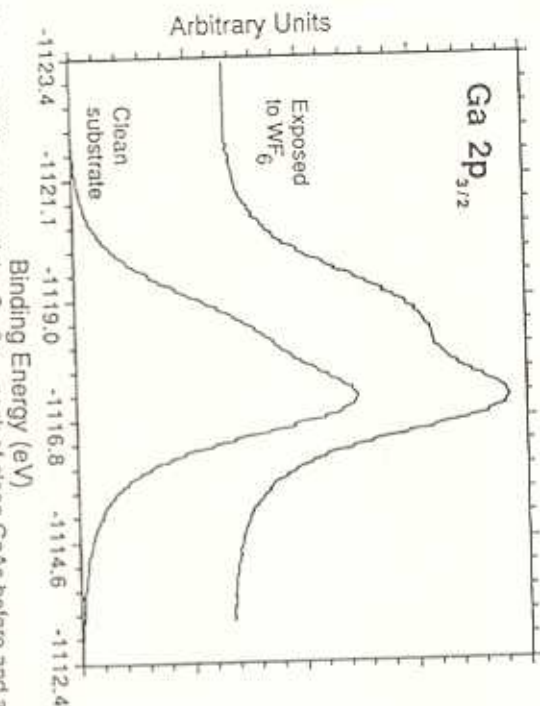


Figure 2. XPS spectra of the Ga $2p_{3/2}$ peak of clean GaAs before and after exposure to 10 Torr of WF_6 for 10 minutes.

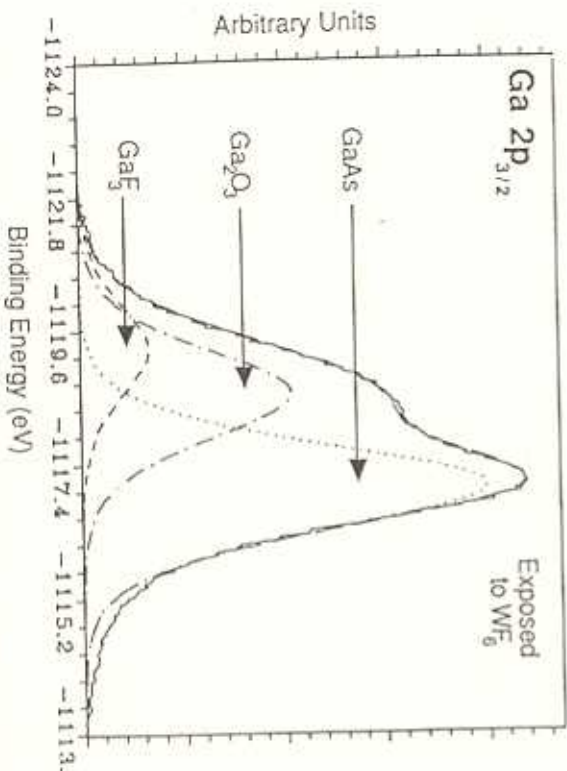


Figure 3. The deconvoluted Ga $2p_{3/2}$ XPS peak after exposure to 10 Torr of WF_6 for 10 minutes.

In another experiment, we exposed clean GaAs to 100 Torr of H_2 and 10 Torr of WF_6 simultaneously, in order to detect any differences due to the presence of the reducing gas. The effects of WF_6 exposure mentioned above are still detected.

To study the effects of the oxides, especially As_2O_3 which seems to play an active role in the reaction, we removed the oxide layer by Ar sputtering (500eV for 10 minutes) and heated the sputtered GaAs sample to a temperature of 550°C to reduce the damage produced by sputtering. This is done in the preparation chamber of the XPS spectrometer, which has a base pressure of less than 10⁻⁹ mbar. In this manner, we obtained a surface free of any arsenic oxides, but some Ga_2O_3 is still present. We then exposed the sample to 10 Torr of WF_6 for 10 minutes, as before. The resulting spectra showed a much weaker adsorption of tungsten fluorides and oxyfluorides but the F/W ratio was still close to 4. The corresponding As and Ga $2p_{3/2}$ peaks did not change after WF_6 exposure. This means that the substrate was much less affected than in previous cases.

One might expect water vapor, the predominant residual gas in our deposition chamber, to play a role in the observed reactions. It is probably responsible for the formation of the tungsten oxyfluorides detected at the surface of the substrates. Residual H_2O might also have an effect in triggering the reaction between WF_6 and As_2O_3 (by partially dissociating WF_6 for example). However H_2O did not cause a reaction between WF_6 and the GaAs surface which was sputtered and subsequently annealed, as noted above.

From our XPS analysis, we conclude that exposure of WF_6 to GaAs in our LCVD experimental conditions leads to a loss of As_2O_3 and to the formation of both GaF_3 and W compounds such as WO_xF_y and WF_x . Since the Ar sputtered GaAs samples which contained no As_2O_3 but some Ga_2O_3 show no GaF_3 formation and a weaker formation of W compounds, we conclude that the primary reaction of WF_6 is with As_2O_3 , producing volatile compounds such as AsF_3 and AsF_5 . However, this oxide etching reaction does not produce metallic W. Instead, the incompletely dissociated WF_x could subsequently attack the unprotected GaAs matrix leading to a loss of As (through the formation of arsenic fluorides) and to the formation of GaF_3 , which is stable and non-volatile at room temperature (8).

DISCUSSION AND CONCLUSION

Using these results and observations, we may suggest the effect this reaction, and more specifically the formation of GaF_3 , can have on the growth of the W film, in our LCVD process. Since WF_6 adsorbs on GaAs and is decomposed by the laser heating of the substrate to form metallic tungsten, we suggest that the formation of GaF_3 prior to laser processing might poison the initiation of a deposition process by forming a layer which is inert to WF_6 . This layer may inhibit the dissociation of WF_6 into metallic W even in the presence of the laser beam and a reducing gas, by increasing the activation energy of the W deposition. We were unable to measure this activation energy, due to the lack of controllability of the process. However, it is interesting to note that the boiling point of GaF_3 is 950°C, a temperature that is never reached by the substrate in any of the stages of the process. Moreover, the GaF_3 formation seems linked to the presence of As_2O_3 and possibly of other surface oxides, that is, to parameters which may readily vary from one experiment to another and possibly from one region to another on the same sample. The effect of GaF_3 on the whole process is still under investigation.

The reaction mechanisms seem very complex and more experiments are needed to clarify the role of the different oxides in this reaction. Only then can reliable and reproducible results of LCVD of W from WF_6 on GaAs be obtained.

ACKNOWLEDGMENTS

One of us (M.T.) would like to thank the Programme de Bourses de la Francophonie for the financial assistance. The authors would like to acknowledge the financial support to the Fonds FCAR and of the Natural Sciences and Engineering Research Council of Canada. We also thank Dr. Edward Sacher and Mrs. Suzie Poulin and Mr. Patrick Desjardins for valuable discussions, and Jean-Paul Lévesque for his technical assistance.

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