

SURFACE INTERACTION BETWEEN Wf_6 AND $GaAs$ UNDER UV LASER ILLUMINATION

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ABSTRACT

We have studied laser-CVD of W on GaAs by X-ray Photoelectron Spectroscopy (XPS). Deposition of W is obtained by irradiating GaAs samples with a KrF excimer laser at normal incidence to the substrate, in a cell containing Wf_6 mixed with H_2 and Ar. We have previously shown that Wf_6 and GaAs react at room temperature even without laser illumination. GaF₃ formation and a loss of As were detected at the surface of the samples by XPS. At laser fluences of 50 mJ/cm², this reaction appears to be enhanced by laser heating of the substrate, but no metallic W is formed. At laser fluences of 67 mJ/cm², metallic W begins to be deposited, through a pyrolytic dissociation reaction with the substrate.

INTRODUCTION

There has recently been considerable interest in depositing W on GaAs using a CVD process with Wf_6 as the metal precursor gas [1-4]. Tungsten [5] and its silicides [6] form thermally stable Schottky contacts on GaAs, and it is therefore used in the high temperature self-aligned gate process. Chemical vapor deposition (CVD) processes have some important advantages over the physical deposition techniques [2,3]. Laser-CVD offers the possibility of deposition in a selective manner, so that resistless laser projection patterning can be achieved, in appropriate circumstances.

We have therefore investigated laser CVD of W from Wf_6 on GaAs using a KrF excimer laser, both with and without H_2 as a reducing gas, and have observed a surface reaction between Wf_6 and GaAs under laser illumination. We have used *in-situ* XPS to study the mechanisms of this reaction. GaF₃ formation and a loss of As were detected at the surface of the samples. Metallic tungsten begins to be deposited at laser fluences of 67 mJ/cm², even when no reducing gas, such as H_2 , was used. The presence of a threshold for metallic W formation suggests that the deposition process is pyrolytic.

EXPERIMENTAL

The W deposition cell is a stainless steel high vacuum five-way cross, evacuated by a rotary pump and a turbomolecular pump, to obtain a base pressure of the order of 10^{-6} Torr. Wf_6 , H_2 , Ar and SiH_4 can be introduced into the cell. The KrF excimer laser ($\lambda = 248$ nm) beam is weakly focused and is incident perpendicular to the sample. The maximum repetition rate of our laser (Lumonics TE-261-2) is 2 Hz and most of the experiments were carried at a repetition rate of 1 Hz. A high vacuum transfer rod is connected to the cell and allows vacuum transfer of the samples from and to an XPS spectrometer (VG ESCALAB3 MkII) which also has an Ar⁺-sputtering gun for sample *in-situ* cleaning. The Al K α radiation (1486.6 eV) from a nonmonochromatized source was used to obtain the XPS spectra.

Semi-insulating LEC GaAs (100) substrates were degreased in boiling trichloroethane, acetone and propanol, then dipped for 5 minutes in DI H_2O and in a hot 1:1 HCl: H_2O solution. The samples were then rinsed for one minute in DI H_2O and dried in flowing nitrogen before being placed in the deposition cell. In some

cases, the samples were Ar⁺-sputtered and then annealed in vacuum to remove the native oxide layer.

All experiments were performed with flowing gas conditions. After the sample was introduced, the chamber was heated to 80 °C under a 100 sccm Ar flow. The process gases (H₂, WF₆ and Ar) were then introduced. Typically, H₂, Ar and WF₆ flows were 10, 10 and 1 sccm. The total pressure was about 40 Torr. Once laser irradiation was completed, the system was pumped to its base pressure and the sample was transferred to the vacuum transfer rod and then to the XPS spectrometer.

RESULTS

We have previously reported [7] a slow room temperature reaction between WF₆ and the GaAs surface, even without any laser irradiation. The formation of GaF₃ and a loss of As were detected at the surface of samples exposed to WF₆. To study the effect of the laser beam on the process, we irradiated the GaAs samples with Krf laser pulses using various laser energy densities and numbers of pulses, in the presence of WF₆ and of H₂-Ar mixtures.

Figure 1 shows the Ga 2p_{3/2} surface sensitive peak (for which the electron mean free path, λ_e , is equal to 0.7 nm) of the clean GaAs surface before (a) and after irradiation with 500 laser pulses at two different energy densities, 50 and 67 mJ/cm² (b and c) in the presence of WF₆ and Ar. A new peak appears at 1119.5 eV after laser irradiation. This corresponds to a shift of 2.3 eV to higher binding energies from the GaAs peak at 1117.2 eV. The appearance of this feature could also be detected on the bulk sensitive, 3d peak ($\lambda_e = 2.5$ nm), with a shift of about 2.5 eV from its position in GaAs. For both peaks, this shift is too large for Ga bonded to oxygen. Ga must therefore be bonded to a more electronegative element, that is, fluorine. This shift is indeed in agreement with the GaF₃ shift detected by Alnot et al. [8]. We therefore attribute this peak to the presence of GaF₃ on our samples after laser irradiation. Moreover, GaF₃ is the only stable Ga fluorinated compound known. In contrast, no fluorinated As compound were detected at the surface of the laser irradiated samples. This can be seen in Fig. 2, which shows the As 3d and W 4f peaks for four different samples: a) clean GaAs, b) GaAs exposed to WF₆, c) GaAs irradiated by 500 laser pulses in an atmosphere of WF₆ and Ar, and d) GaAs irradiated by 500 laser pulses in an atmosphere of WF₆ and H₂. The only As species detected are As bonded to Ga (at 41.1 eV), elementary As (at 41.8 eV), which cannot be resolved from the GaAs contribution) and As oxide (at 44.2 eV). There is loss in stoichiometry at the surface of the laser treated samples. The As/Ga ratio, calculated from the 2p_{3/2} peaks, goes from 1.04 before laser irradiation to about 0.66 for the 50 mJ/cm² and to 0.44 after 67 mJ/cm² treatment.

To understand the effect of laser irradiation on formation of metallic W, we have analysed the W 4f peaks in Figure 2. For sample b, the W signal is a small feature observed at 37 eV. This has already been reported in a previous publication [7], where it was shown that WF_x and WO_yF_x (with x=4) adsorb on GaAs following WF₆ exposure. For samples c and d, the signal due to the W 4f peak increases and the feature enlarges towards lower binding energies. The ratio of the W 4f signal to Ga 3d signal of the substrate, goes from 0.05 (sample b) to about 0.15 for samples c and d. These observations suggest that some dissociation of the tungsten fluorinated species at the substrate surface has taken place under the influence of the laser beam, and the presence of H₂ does not seem to make a major difference.

In order to study the effect of the native oxide layer (estimated to be 7 Å) on the observed reactions, this layer was removed by Ar⁺-sputtering (E=500eV). The sample was then annealed in vacuum (550 °C for ten minutes). Under laser irradiation in a WF₆-Ar ambient, the GaF₃ formation and the loss of As were still

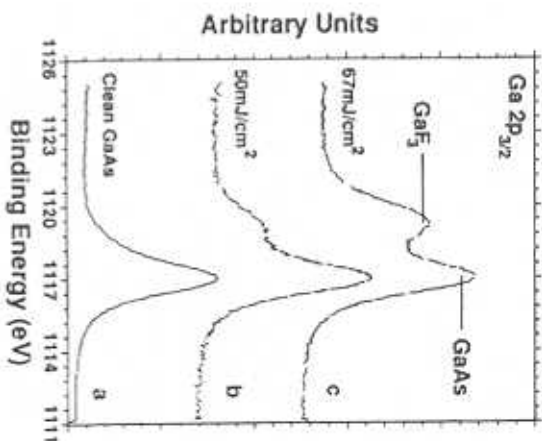


Figure 1. XPS spectra of the Ga 2p_{3/2} peak before and after irradiation by 500 laser pulses for different laser energy densities.

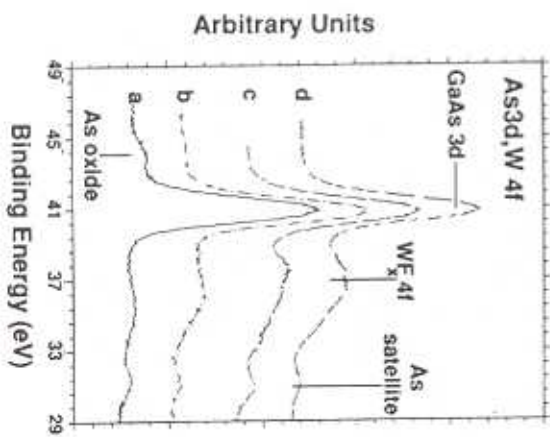


Figure 2. XPS spectra of the As 3d and W 4f peaks for: (a) the clean GaAs surface, (b) after exposure to WF₆ after 500 laser pulses (50 mJ/cm²) in a WF₆ atmosphere (c) without H₂ and (d) with H₂.

detected as the W/GaAs ratio was close to 0.15. This shows that the reaction is with the GaAs matrix and not only with the native oxide.

Up to this point, no metallic tungsten was detected, since the corresponding peak should be at about 31 eV. Figure 3 (a) shows the W 4f peak region for a sample irradiated with 3000 laser pulses with an energy density of 67 mJ/cm², in an ambient of WF₆ and Ar. We observe that the W signal has increased significantly, and that it has shifted towards the metallic tungsten position. However, we also should note that a substantial amount of fluorinated W is still present. After 7300 laser pulses at 67 mJ/cm², Figure 3 (b), the metallic tungsten 4f peaks are finally detected, as they appear as a well separated doublet at 31.50 eV and 33.65 eV, and the signal from the substrate has diminished substantially. This last sample was transferred under ambient air, leading to the presence of the tungsten peaks at 35 and 37 eV, corresponding to tungsten oxides. For samples irradiated with more than 7000 laser pulses, metallic tungsten formation was detected, even when no H₂ reducing gas was introduced with WF₆ into the reaction chamber.

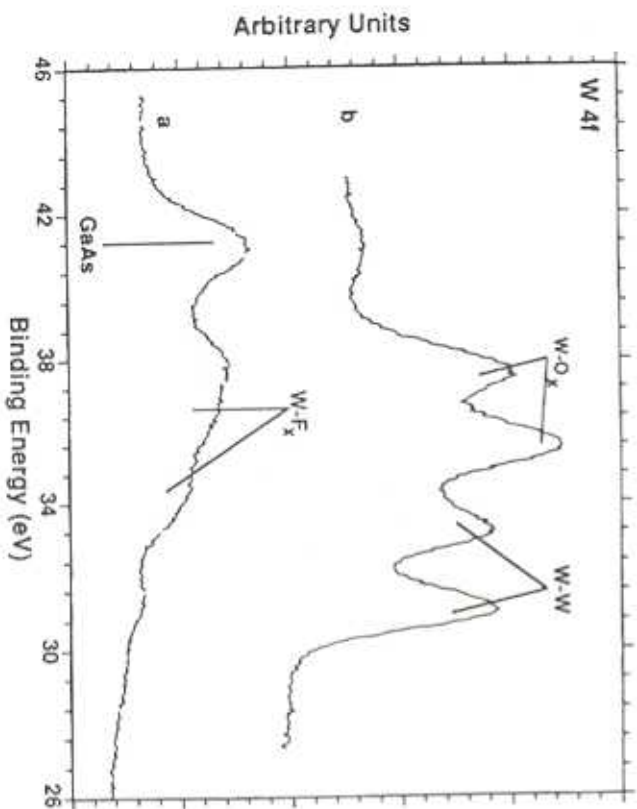


Figure 3. XPS spectra of the W 4f and As 3d peaks after laser irradiation by (a) 3000 and (b) 7300 laser pulses with an energy density of 67 mJ/cm².

DISCUSSION

As the laser beam strikes the GaAs substrate in an WF₆ ambient, the formation of GaF₃ and the loss of As enhanced, as shown by our XPS analysis. These are detected after 500 pulses, before any metallic W is formed, and they become more evident as the laser pulse energy density (and the substrate temperature rise due to the incident laser beam) is increased. As the number of laser pulses is increased, the dissociation of the fluorinated tungsten species at the surface of the sample increases and metallic tungsten is detected after about 7300 laser pulses at 67 mJ/cm², even in the absence of H₂. We therefore conclude that under laser irradiation, metallic tungsten can be formed through dissociation of WF₆ with the substrate.

No gas phase photo-dissociation of WF₆ is to be expected for KrF excimer laser radiation ($\lambda = 248$ nm). WF₆ absorbs at 225 nm and below [9]. The KrF laser, 5 eV, photons do not have enough energy to strip a fluorine atom from the WF₆ molecule (as this requires about 5.3 eV [9]). Photo-dissociation of adsorbates is not automatically excluded as their electronic spectra can be quite different from the molecule in the gas phase. However, no metallic tungsten was detected for samples irradiated with 6300 laser pulses with an energy density of about 67 mJ/cm², H₂/Ar ambient. Thus there is little photochemical contribution to WF₆ dissociation. The process must be pyrolytic, with a threshold energy density of about 67 mJ/cm². A rough calculation of the temperature increase due to an 8 nsec, KrF excimer laser pulse gives a value of about 420 °C. The steady state temperature change is negligible at the relatively low 1 Hz laser repetition rate used. At such temperatures, we do not expect any thermal decomposition of GaAs. Therefore, the loss in As may be explained by the formation of volatile AsF₃ and AsF₅. GaF₃ is stable, and the temperature rise due to the laser beam is not high enough to cause its sublimation [7]. The presence of fluorine bonded to Ga in such a stable manner reduces the number of available sites on which WF₆ can adsorb to undergo dissociation and therefore nucleation of metallic tungsten films becomes difficult, as reported by some authors [1, 3]. However, if the temperature increase is high enough, metallic W can be formed. At this point, W CVD on the pre-existing W layer can proceed through the H₂ reduction of WF₆. However, the presence of H₂ does not seem to affect the initial surface interaction between WF₆ and the substrate, but its effects on the subsequent growth of the metallic film and its properties still need to be clarified.

CONCLUSION

We have investigated the initial stages of W laser-CVD on GaAs using WF₆ as the metal precursor gas, and a KrF excimer laser, incident perpendicular to the substrate's surface, as a photon source. By using *in-situ* XPS, we have shown evidence of a surface reaction between WF₆ and GaAs leading to GaF₃ formation and to a loss of As on the GaAs surface. This reaction is enhanced as the laser energy density is increased. At a subsequent stage, metallic W formation is detected above a threshold value of the laser energy density (near 67 mJ/cm²). This appears to be caused by the laser induced temperature rise at the surface of the substrate.

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REPAIR OF FLAT PANEL DISPLAY SUBSTRATES BY LASER DIRECT WRITING OF METALLIC PLATINUM, COPPER AND ALUMINUM AND INSULATING ALUMINUM OXIDE UTILIZING GAS PHASE REACTANTS

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ABSTRACT

The identification and repair of defects in flat panel displays (FPDs), most especially liquid crystal, are required to achieve acceptable manufacturing yields and reasonable costs. Laser cutting and laser direct writing, from gas phase reactants, are used to repair opens and shorts in conductor lines of FPD substrates (the L1 laser repair system). This paper details platinum, copper and aluminum deposition processes including deposition parameters, conductivity data, Auger evaluations and microscopy characterizations. Life-study data on repaired, fully assembled FPD's will be presented. Also the laser direct-writing process for aluminum oxide, used to repair dielectric defects and to passivate metal repairs, will be described. Finally, a unique, localized vacuum system (SPOT VAC™), specifically engineered for laser deposition on large (500 X 500mm) flat substrates, will be detailed.

1. INTRODUCTION

The development of inspection, testing and defect repair of active matrix liquid crystal displays (AMLCD's) is required to raise manufacturing yields from the present 10-40 percent to a level whose mass-marketing applications such as notebook computers and HDV are economical. We have developed a repair system (the L1 system) for flat panel displays which utilizes laser cutting and laser deposition technologies [1,2] to repair line opens, line shorts and cross-over shorts in bus lines. The success of the L1 approach has been exemplified in a recent publication [3] which describes the repair and subsequent satisfactory operation of color, high definition, liquid crystal displays. Our initial deposition processes were the laser direct writing of conductive cobalt [4,5,6] and insulating cobalt oxide [6] lines from gas phase reactants. As the variety in LCD materials and cleaning procedures (for example, substrate cleaning processes) expanded, we developed additional deposition processes, namely Pt[6], Cu and Al, to repair LCD's. Additionally, Cu and Al were developed with an eye towards the modification and repair of advanced device packages, such as multi-chip modules.

An additional concern now being expressed by AMLCD manufacturers is that repairs to fully fabricated panels will subsequently leave the repaired sites exposed to the liquid crystal medium, a potentially undesirable situation. In response to this concern, we will also report on our present development of aluminum oxide deposition which can be used to isolate these repaired sites from the liquid crystal medium.