Laser induced deposition of tungsten on GaAs from WF_6

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Laser induced deposition of tungsten from WF_6 on GaAs using a focused continuous wave scanning argon-ion laser was investigated. Deposits were prepared with H_2 as a reducing agent, as well as without it. Deposition of tungsten is found to occur in a narrow process window, suggesting the existence of a competing etching reaction. Film composition and structure were analyzed by scanning electron microscopy and Auger electron microscopy. Surface reactions were studied by x-ray photoelectron spectroscopy. The data suggest that the GaAs surface participates in the reaction with WF_6, leading to the formation of GaF_3 which may poison the initiation of the deposition process.

I. INTRODUCTION

Interest in laser direct writing of conductive materials for circuit modification for very large scale integrated applications has increased in recent years.[1-3] An appropriate process for such an application is laser induced chemical vapor deposition (LCVD), which is a pyrolytic process using a focused laser beam as a heat source. Tungsten is a low resistivity refractory metal of interest for microelectronics applications. It is especially interesting for GaAs technology since W is known to form a good Schottky contact on that compound.[4,5] It can be deposited through the reduction of WF_6. However, WF_6 is not commonly used for processes involving GaAs. Its use in such cases has been reported only for plasma-enhanced CVD (PECVD)[6] and for focused ion beam deposition.[7] Prior to the work of our group, laser deposition of W on GaAs had been reported only for a photolytic process using $W(CO)_6$.[8] Recently, low temperature CVD of W, through H_2 reduction of WF_6[9] and laser induced deposition of W by SiH_4 reduction,[10] has been reported. These results suggest that deposition processes such as these, might be used on thermally sensitive substrates, such as GaAs. We present here a study of the deposition of W from WF_6 on GaAs using a continuous wave (cw) argon-ion laser beam. Lines were deposited in a narrow process window and were difficult to reproduce. In some cases, deposits were 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).

II. EXPERIMENT

The deposition system consists of a cw argon-ion laser beam focused onto the substrate using a long working distance microscope objective with a numerical aperture of 0.15. Operating the laser at 514 nm, the maximum power available at the substrate is 1.3 W. The spot size at e^{-2} in intensity, measured by the scanning knife-edge technique,[11] is 3.7 μm. The substrate was placed in a 10 cm^3 stainless-steel reaction chamber, pumped to a base pressure of $\approx 10^{-2}$ Torr by a mechanical pump. The cell window is made of fused silica. The reaction chamber is mounted on computer-controlled X–Y translation stages having a spatial resolution of 0.1 μm and a maximum velocity of 100 μm/s. The substrates were (100) semi-insulating liquid encapsulated Czochralski GaAs. They were degreased in hot trichloroethane, acetone, and propanol, rinsed in deionized (DI) water, and then etched in H_3PO_4:H_2O_2:H_2O (1:1:10) for 5 s. Samples were then rinsed in hot HCl:H_2O (1:1) for 5 min and then in DI water and dried in flowing nitrogen. Prior to deposition, the cell was heated to 80 °C and purged with an Ar flow of 100 sccm during 1 h. The substrate temperature during deposition was $\approx$30 °C. Scanning electron microscopy (SEM) and Auger electron spectroscopy (AES) depth profiling were used to characterize the morphology and composition of deposited lines. The surface reactions between WF_6 and GaAs were studied by XPS in conditions similar to those of deposition.

III. RESULTS

As GaAs is a thermally sensitive compound, we first determined the maximum power which can be used without damaging the substrate. In this work, damage is defined as a morphological modification of the GaAs surface that is visible under white light using 80× magnification. The damage threshold power (DTP) is defined as the minimum power at which such damage is observed. Damage can be either in the form of hillocks or of trenches.[12] Figure 1 shows the DTP as a function of pressure for argon and hydrogen when the velocity is 25 μm/s. It increases with pressure up to $\approx$3 Torr and then appears to saturate. The DTP is the same for Ar and H_2. However, it is strongly affected in the presence of WF_6. Note that with WF_6, the DTP is even lower than that observed in vacuum. Using a contact profiler (Dektak 3030), it was found[12] that, in the presence of WF_6, trenches are formed at 75 mW, whereas hillocks are formed at higher power, in the absence of WF_6. This suggests the possibility that WF_6 etches GaAs, producing volatile compounds such as AsF_3 and AsF_5. From the steady-state calculation of Nissim *et al.*,[13] where the temperature dependence of the thermal conductivity has been taken into consideration, we evaluate the surface temperature of GaAs to be $T \approx 400$ °C for $P = 75$ mW. Note

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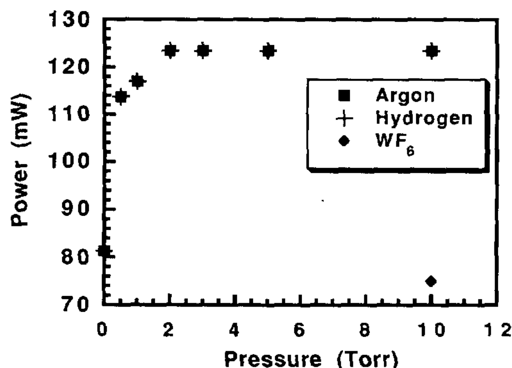


FIG. 1. Damage threshold power as a function of gas pressure and composition. Beam diameter is 3.7 μm at $1/e^2$ of maximum intensity.

that this is below the onset temperature for thermal decomposition of GaAs, believed to be 650 °C. This also suggests that there is a chemical reaction between WF_6 and GaAs. We shall return to this point later.

We investigated the deposition of W onto GaAs using WF_6 only, as well as mixtures of WF_6:H_2. To avoid any damage to the substrate, we applied only laser power below the DTP determined in the damage study. Figure 2 shows the deposit thickness as a function of laser power for gas mixtures of WF_6:H_2 and for WF_6 alone. The writing speed is 25 μm/s in both cases. The deposit thickness is usually less than 100 nm and decreases above a certain laser power, showing a competition between deposition and etching mechanisms. This leads to deposition in a very narrow process window, about 10 mW wide. Deposits are also difficult to reproduce even on the same substrate. The temperature corresponding to the lowest power producing a deposit, 57 mW, is estimated to be about 300 °C. Figure 3 shows SEM micrographs of W lines deposited using (a) a gas mixture of WF_6:H_2, and (b) with WF_6 alone. The lines deposited using H_2 are granular. This morphology seems similar to the one reported by Gilgen *et al.*[8] for W films deposited photochemically on GaAs from $W(CO)_6$. For the lines deposited without H_2 the morphology is relatively smoother, as shown in Fig. 3(b).

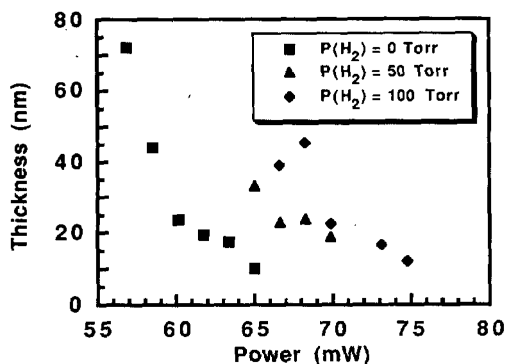
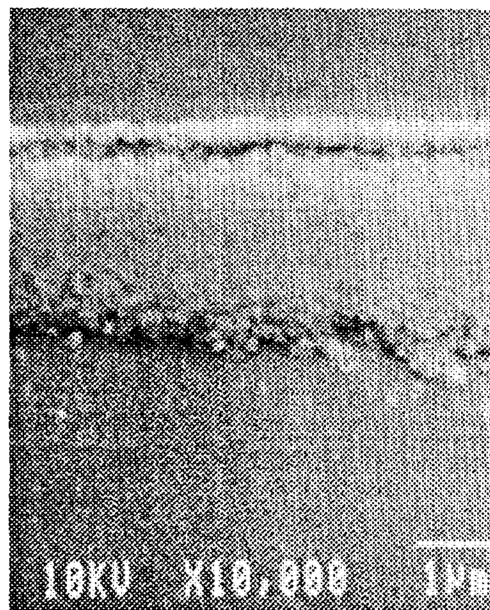
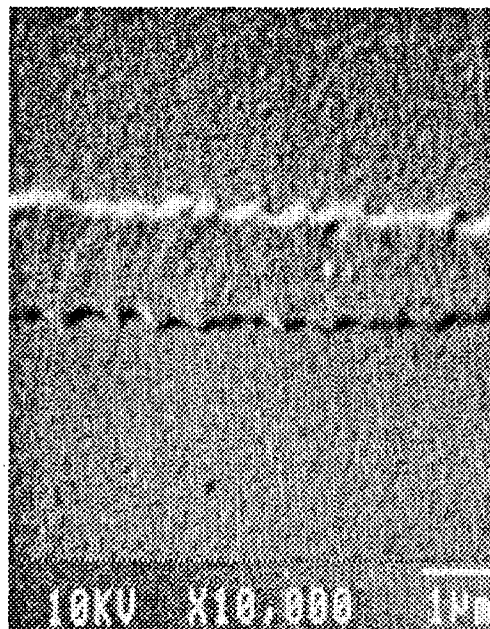


FIG. 2. Thickness of deposited lines as a function of incident laser power for different gas compositions with a constant partial pressure of WF_6 of 10 Torr. The writing speed is 25 μm/s.



(a)



(b)

FIG. 3. (a) SEM image of a line deposited with 50 Torr of WF_6 and 10 Torr of H_2. (b) SEM image of a line deposited with 10 Torr of WF_6. In both cases the writing speed is 25 μm/s.

Figure 4 shows AES depth profiles of lines deposited using (a) a mixture of WF_6:H_2, and (b) WF_6 without reductant gas. Both deposits contain only about 30% tungsten. In addition, a very high incorporation of As is noted through all the deposit for the case where no reductant gas is used. When H_2 is used, this As incorporation is still observed, but to a lesser extent. Another difference between the two spectra is the presence of a more important Ga diffusion up to about 50 nm in the deposit when no H_2 is present during the deposition process. The deposition process appears to be very complex. However, the AES profiles seem to indicate the presence of two different regimes. The first regime is characterized by As and Ga incorporation in the depositing film, and takes place in both types of

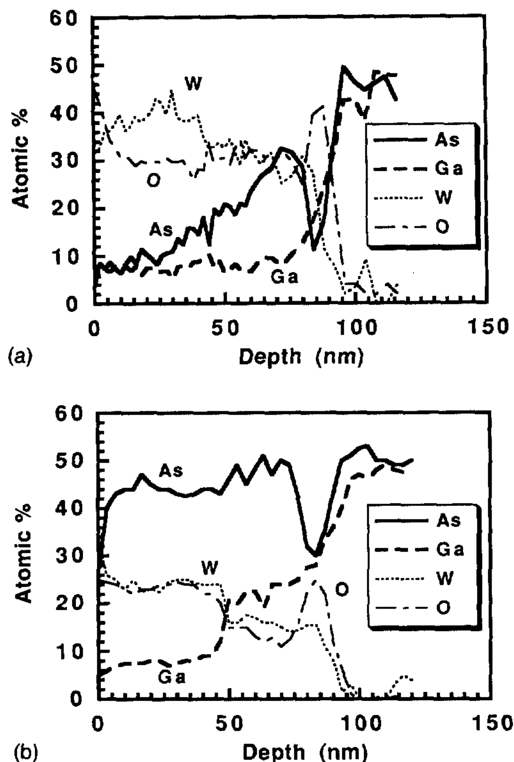


FIG. 4. AES profile of a lines deposited with 10 Torr of WF_6 and (a) 50 Torr of H_2 and (b) 0 Torr of H_2. (Note that C was also present, probably due to the incorporation of hydrocarbons after deposition. It has been removed from the profiles for clarity.)

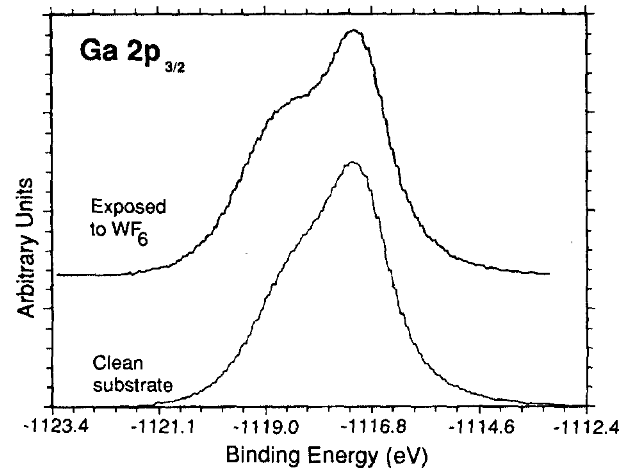


FIG. 5. XPS $2p$ 3/2 peaks of Ga before and after exposure to 10 Torr of WF_6 for 10 min.

deposits. It can be associated with a reduction of the WF_6 by the GaAs surface (otherwise, there would not be any deposits in the absence of H_2). The second regime probably involves the reduction of WF_6 by H_2 under laser irradiation. This reaction seems to become predominant as the film grows, and this can explain the reduced residual incorporation of As in the film when H_2 is used as a reducing gas. In this case, the high As content layer becomes partially buried in the film. However, due to the short dwell time for the growth process (148 ms) the second regime never completely overcomes the first. More work has to be done to fully understand these processes.

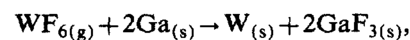
Oxygen is present throughout films deposited on GaAs. This is probably due to the fact that these very granular films were exposed to air before surface analysis was performed. Even if surface oxides play a role in the deposition process, it is unlikely that they supply this amount of oxygen in the deposit. Furthermore, no oxygen in the bulk was detected by AES[14] in tungsten films deposited on silicon oxynitride in the same system, suggesting that O is not incorporated during growth. The oxygen peak in both films, at about 80 nm from the surface, is attributed to the oxide present at the GaAs surface before deposition.

IV. DISCUSSION

We suggest that the presence of As in the film cannot be due to As atoms evaporated by the laser from the GaAs surface and then trapped in the film during growth. If this were so, a gallium-rich surface should be expected under the deposited film. This is not the case, as may be seen from the AES depth profiles of Fig. 4. Furthermore, the GaAs surface has not been rebuilt from the bulk, since a simple calculation shows that As diffusion coefficients on the order of 10^{-10} cm^2/s would be required for this. This is much larger than the highest reported value, of 10^{-14} cm^2/s (Ref. 15) at 850 °C (a considerably higher temperature than estimated to occur here). The As incorporation must therefore be due either to a surface diffusion process or to a gas phase As volatile compound produced by a spontaneous reaction between WF_6 and the GaAs surface. For the moment, both explanations are possible and experiments are underway to determine the most probable mechanism in the process.

XPS studies were undertaken in order to explore the interaction of WF_6 with GaAs. Measurements were performed in a VG ESCALAB Mk II using the Al$K\alpha$ x-ray line. A transfer module has been used to carry the sample in vacuum from the process chamber to the surface instrument, in order to avoid air exposure before analysis.

Samples of GaAs were exposed to 10 Torr of WF_6 during 10 min at room temperature, in order to investigate whether a reduction reaction occurs between GaAs and WF_6. Among the possible reactions, the one which appears most likely, due to a large enthalpy change (the free energy changes are not generally known) is:[16]



$$WF_{6(g)} + 2Ga_{(s)} \rightarrow W_{(s)} + 2GaF_{3(s)},$$

$$\Delta H = -98.5 \text{ kcal/mol.}$$

If this is in fact the case, we should observe the presence of GaF_3 at the surface of GaAs after exposition to the WF_6. Figure 5 shows the Ga $2p$ 3/2 peak before and after exposure to WF_6 (the $2p$ peaks are more surface sensitive than the $3d$ peaks[17]). The presence of GaF_3 after exposure is indicated by the appearance of a shoulder indicating the presence of a new peak, shifted by 2.1 eV toward higher binding energy. This corresponds to bonding to a more electronegative element, such as fluorine, and confirms the hypothesis of a reaction between WF_6 and GaAs occurring

at room temperature. Quantitative analysis of the shifted Ga peak intensity and of the F peak intensity indicates a Ga:F ratio of $\sim 1:3$. No AsF_x was observed on the surface. The various components of the XPS spectrum and the details of the analysis are presented elsewhere.[17]

This reaction, and more specifically the formation of GaF_3, may have a major influence upon the growth of the W film in the LCVD process. WF_6 adsorbs on GaAs and is decomposed by laser heating of the substrate to form metallic tungsten. We suggest that the formation of GaF_3 prior to laser processing may poison the initiation of the 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. Further details concerning this reaction have been presented elsewhere.[17] Further work on this problem is in progress.

V. CONCLUSION

We have presented experimental results on laser-induced deposition of W from WF_6 on GaAs. Deposition of W was achieved without using any reductant gas, suggesting that GaAs plays a role in the deposition mechanism. AES depth profiles show significant incorporation of As in the film. XPS analysis shows the presence of GaF_3 at the surface of GaAs after exposure to WF_6 at room temperature. We suggest that this is formed during spontaneous reduction of WF_6 by the GaAs surface.

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[1]Y. Nambu, Y. Morishige, and S. Kishida, Appl. Phys. Lett. **56**, 2581 (1990).

[2]J. Y. Lin and S. D. Allen, *In-Situ Patterning: Selective Area Deposition and Etching*, edited by A. F. Bernhardt, J. G. Black, and R. Rosenberg (Materials Research Society, Pittsburgh, PA, 1990), Vol. 158, p. 85.

[3]J. G. Black, S. P. Doran, M. Rothschild, and D. J. Ehrlich, Appl. Phys. Lett. **50**, 1016 (1987).

[4]S. P. Kwok, J. Vac. Sci. Technol. B **4**, 1383 (1986).

[5]J. Y. Josefowicz and D. B. Rensch, J. Vac. Sci. Technol. B **5**, 1707 (1987).

[6]J. Wood, Appl. Surf. Sci. **38**, 397 (1989).

[7]Z. Xu, T. Kosugi, K. Gamo, and S. Namba, Jpn. J. Appl. Phys. **29**, L23 (1990).

[8]H. H. Gilgen, T. Cacouris, P. S. Shaw, R. R. Krchnavek, and R. M. Osgood, Appl. Phys. B **42**, 55 (1987).

[9]C. M. McConica and K. Krishnamani, J. Electrochem. Soc. **133**, 254 (1986).

[10]J. G. Black, S. P. Doran, M. Rothschild, and D. J. Ehrlich, Appl. Phys. Lett. **56**, 1072 (1990).

[11]D. K. Cohen, B. Little, and F. S. Luecke, Appl. Opt. **23**, 637 (1984).

[12]A. Lecours, R. Izquierdo, and M. Meunier, Appl. Surf. Sci. **54**, 60 (1992).

[13]Y. I. Nissim, A. Lietoila, R. B. Gold, and J. F. Gibbons, J. Appl. Phys. **51**, 274 (1980).

[14]R. Izquierdo, A. Lecours, and M. Meunier, *Photon and Low Energy Particles in Surface Processing*, edited by C. I. H. Ashby, J. H. Brannon, and S. W. Pang (Materials Research Society, Pittsburgh, 1992), Vol. 236, p. 111.

[15]S. M. Sze, *Semiconductor Devices: Physics and Technology* (Wiley, New York, 1985).

[16]A. Lecours, M. Sc. A. thesis, Ecole Polytechnique de Montréal, 1991 (unpublished).

[17]M. Tabbal, A. Lecours, R. Izquierdo, M. Meunier, and A. Yelon, *Photon and Low Energy Particles in Surface Processing*, edited by C. I. H. Ashby, J. H. Brannon, and S. W. Pang (Materials Research Society, Pittsburgh, 1992), Vol. 236, p. 117.