Laser-chemical vapor deposition of W Schottky contacts on GaAs using WF_6 and SiH_4

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Tungsten was deposited on GaAs using a low-temperature laser-chemical vapor deposition process. A KrF excimer laser beam incident perpendicularly on a GaAs surface was found to induce metallic W formation from a gas mixture containing WF_6 and SiH_4 at laser energy densities as low as 25 mJ/cm^2. *In-situ* x-ray photoelectron spectroscopy analysis shows that SiH_4 plays an important role in the initiation of metallic W deposition at such low laser energy densities. Scanning electron microscopy of the W films shows a dense and regular columnar structure. Auger depth profiles show that the deposited W is pure. No impurities such as F, C, or O were observed, with a detection limit of 1 at. %, and the interdiffusion between W and GaAs is minimal. X-ray diffraction shows that the W film is mostly in the stable, highly conductive α phase, as confirmed by the low resistivity value of 21 $\mu\Omega$ cm. Metallic W features of 60 μm on GaAs were obtained by laser direct-projection patterning. $I-V$ measurements show that the W–GaAs structures formed provide good quality Schottky contacts, with an average barrier height of 0.71 eV and an average ideality factor of 1.2. To our knowledge, these are the first Schottky diodes obtained using a laser based resistless projection patterning process on GaAs. © *1997 American Institute of Physics.* [S0021-8979(97)07410-0]

I. INTRODUCTION

The use of *in situ* resistless processes in all-dry integrated chambers is particularly advantageous for the fabrication of GaAs integrated circuits due to the fragility of this substrate and to the absence of a stable native oxide.[1] The directionality of the laser beam and the short wavelength of the ultraviolet (UV) photons make it possible to form micron and submicron features on the substrate through projection patterning using a mask placed outside the process chamber.[2] The use of photoresists and the handling of wafers may be eliminated, thus minimizing two major sources of microcontamination. While excimer lasers have been used for *in situ* doping and etching of GaAs has been achieved recently,[3,4] their application to gate metallization for GaAs metal–Semiconductor field effect transistor (MESFET) fabrication remains unexplored. Al,[5] Au,[6] Cr,[7] and Ag, (Ref. 8) have been deposited by excimer projection patterning on GaAs, but none of these metals is thermally stable on GaAs at temperatures higher than 850 °C, which is required for the self-aligned gate MESFET (SAG-MESFET) fabrication process. For this application, tungsten (W) is the metal of choice.[9] It is now widely used as a low resistivity, chemically stable refractory metal contact to GaAs.

Chemical vapor deposition (CVD) of W from WF_6 permits the deposition of high quality W layers containing very little C or O contaminants as compared to films deposited from $W(CO)_6$.[10] Under appropriate conditions, a thermally activated W-CVD process using WF_6 allows single step selective W deposition on Si but not on SiO_2.[11] Most workers have used H_2 to reduce WF_6 into metallic W at temperatures of the order of 400 °C.[12] However, the use of SiH_4 as a reducing gas for WF_6 has been found to lower the W deposition initiation temperature for the WF_6/SiH_4 mixture.[13] For example, Black *et al.*[13] used an Ar^+ laser to deposit W onto polyimide from a WF_6/SiH_4 mixture. They estimated that the initiation of the deposition process takes place at a temperature as low as 175 °C. Desjardins and co-workers[14] deposited WSi_x on TiN from WF_6 and SiH_4 by using the limited laser power density available from an AlGaAs diode laser emitting at 796 nm. These results indicate that the WF_6/SiH_4 gas mixture could be more suitable than the WF_6/H_2 for W deposition on chemically reactive and thermally sensitive substrates such as GaAs or other III–V semiconductors. This is particularly the case for GaAs which has been shown to react with WF_6.[15–19] This interaction can block the nucleation of the W layers and leads to poor quality W films.[18,19] The use of the low-temperature reduction of WF_6 by SiH_4 could limit the interaction of WF_6 with the substrate and still induce the deposition of W films.

We report here on the KrF excimer laser deposition of W from WF_6 and SiH_4 on GaAs. First, the surface interaction between the WF_6/SiH_4 gas mixture and GaAs as studied by x-ray photoelectron spectroscopy (XPS) is discussed. Then, the laser deposited W films are characterized by scanning electron microscopy (SEM), x-ray diffraction, Auger electron spectroscopy, and four-point probe measurements. Finally, we present the properties of the W Schottky diodes on GaAs obtained using our process with laser projection patterning.

II. EXPERIMENT

The deposition system used for this work was presented elsewhere.[19,20] We used a KrF excimer laser beam (MPB

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AQX-150, 0–60 Hz, 150 mJ per pulse) slightly focused at perpendicular incidence onto a GaAs substrate that was placed in a high vacuum stainless steel cell having a base pressure lower than 10^{-6} Torr. Using a high vacuum transfer rod, the samples may be examined in an XPS spectrometer for surface analysis before and after laser treatment. Substrates may also be Ar sputtered and annealed in vacuum in the XPS spectrometer before deposition.

The gas flows used in this work were 1 sccm of WF_6, 3 sccm of SiH_4, 50 sccm of H_2, and 140 sccm of Ar at an operating pressure of 14 Torr. A value of 1:3 for the WF_6/SiH_4 gas flow ratio has proved to be the most suitable for obtaining reproducible W deposits in our experiments.[21] The Ar gas flow was used for two purposes: to purge the quartz window through which the laser beam passes in order to minimize W deposition on it, and as a carrier gas. Dilution of the WF_6/SiH_4 gas mixture with an inert gas is necessary since it is strongly reactive. Uncontrolled reactions leading to particle generation[22] and even to explosive conditions[13] have been reported by some authors.

The substrates were 1 cm^2 squares of Si-doped (10^{17} cm^{-3}) liquid encapsulated Czochralski-grown (100) GaAs. Prior to deposition, they were degreased in the hot solvents, trichloroethane, acetone, and propanol, rinsed in de-ionized (DI) water, dipped in a hot 1:1 HCl:H_2O solution, rinsed again in DI water, and finally dried in flowing nitrogen. They were mounted onto a copper sample holder and introduced into the deposition cell through a loadlock without breaking the vacuum in the system. In some cases, heating (550 °C) of the samples under vacuum ($<10^{-7}$ Torr) in the XPS spectrometer and transfer to the deposition cell under vacuum were carried out in order to remove the residual water vapor found on the samples after the chemical cleaning. The gases were then introduced and the laser was switched on to induce W deposition. The laser energy density was varied between 0 and 40 mJ/cm^2. All XPS spectra were taken using the 1486.6 eV Al K_α ray of the x-ray source on the VG ESCALAB 3 MkII x-ray photoelectron spectrometer.

III. RESULTS

A. Surface interaction between GaAs and the WF_6/SiH_4 gas mixture under laser irradiation

Figure 1 shows the W 4f XPS spectrum of a W deposit obtained by irradiating a GaAs sample by 3000 laser pulses at 25 mJ/cm^2. The detection of a well-resolved doublet at -31.5 and -33 eV indicates that the W formed at the surface of the sample is indeed metallic. This confirms that lower laser energy densities are needed to form metallic W using SiH_4 rather than using H_2 as a reducing gas for WF_6, since we have already shown that the threshold for hydrogen reduction of W under KrF excimer laser irradiation is found at 67 mJ/cm^2. Figure 2 shows the 2p Si XPS spectral window for the same sample. The two peaks detected at -104.5 and -108 eV are attributed to the 3p doublet of Ga in the GaAs substrate. The peak at -99.7 eV is the signal from the 2p orbitals of Si. We can therefore conclude that some SiH_4 has reacted with WF_6, leaving some Si on the surface.

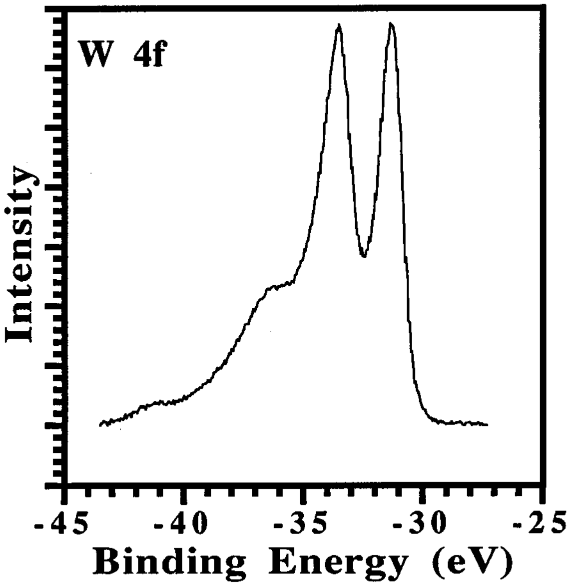

FIG. 1. W 4f XPS spectrum of a deposit prepared from a WF_6/SiH_4 gas mixture.

In order to clarify the role of the adsorbed Si in the formation of metallic W, GaAs samples were exposed to a $SiH_4/Ar/H_2$ mixture with and without laser irradiation at 25 mJ/cm^2. These samples were transfered under vacuum to the XPS spectrometer for analysis. No Si signal was detected on these samples. This indicates that SiH_4 alone does not adsorb on or react with GaAs, even under laser irradiation at 25 mJ/cm^2. XPS was also performed on GaAs exposed to $WF_6/SiH_4/Ar/H_2$ (1:3:140:50) without laser irradiation.

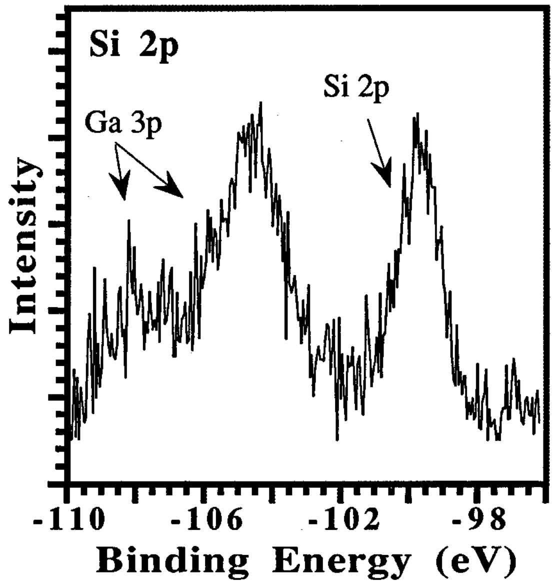

FIG. 2. Si 2p XPS spectrum from a sample irradiated with 3000 laser pulses at 25 mJ/cm^2 in a $WF_6/SiH_4/H_2/Ar$ gas mixture.

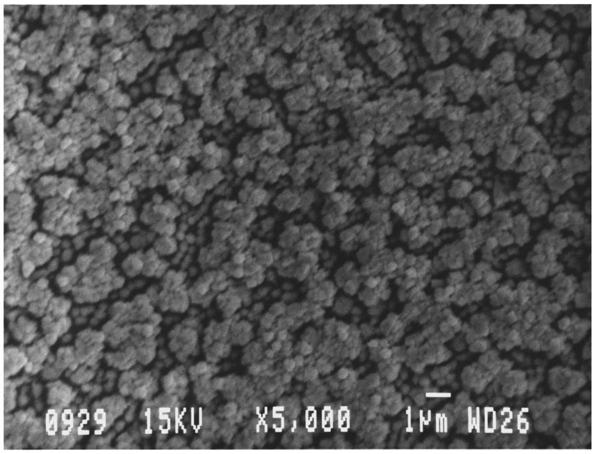

FIG. 3. SEM of a W deposit obtained at 25 mJ/cm^2 (top view).

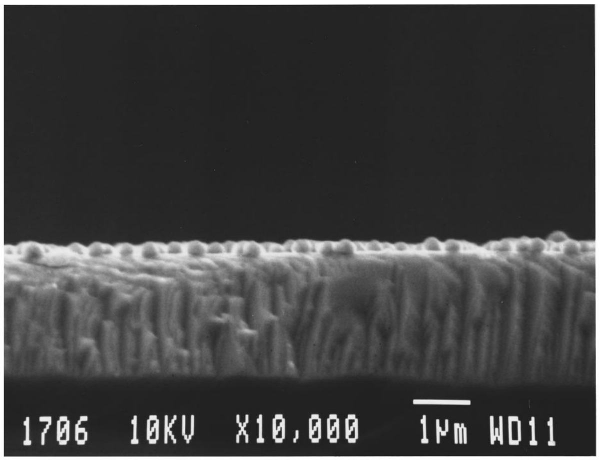

FIG. 4. SEM of a W deposit obtained at 25 mJ/cm^2 (transverse view).

The results are essentially the same as those obtained with room temperature exposure of GaAs to a WF_6/Ar mixture.[17,23] Adsorption of fluorinated W species is detected but no Si species are present at the surface of the substrate. We may conclude that, in these conditions, there is no reaction between SiH_4 and WF_6 and no SiH_4 adsorption on GaAs at room temperature. We deduce that laser irradiation at 25 mJ/cm^2 induces reactions between WF_6 and SiH_4, leading to the formation of metallic W on GaAs.

B. Laser deposition of W from WF_6 and SiH_4 on GaAs

At laser fluences of 19 mJ/cm^2 and below, no metallic W formation was detected, even after 1 h of laser irradiation of the substrate at 60 Hz. After such long exposure to WF_6 and SiH_4, we detected some formation of powder on the substrates. This is most probably due to reactions in the gas phase. Sometimes, powder formation was observed as the two gases were flowed through the cell, with no laser exposure. In such cases, the experiment was interrupted. This phenomenon is due to some accidental variations in the flows of the gases when the flowmeters were switched on at the start of an experiment. This demonstrates the care that must be taken when manipulating this mixture. At laser fluences above 30 mJ/cm^2, the formation of metallic W was detected after 1 min of laser irradiation at 30 Hz (1800 pulses only). However, the films were nonuniform and exhibited very poor adhesion to the substrate, delaminating soon after, or even during, deposition.

Uniform, continuous metallic W layers were obtained at laser energy densities between 23 and 30 mJ/cm^2. At 25 mJ/cm^2, 0.4 μm W layers were deposited after laser irradiation at 30 Hz for 340 s. It is difficult to evaluate the exact deposition rate, since we have noted an incubation time, typically 100 s, before observing a shiny tungsten surface on the samples. On the average, we estimated a deposition rate of 1 nm/s at 30 Hz. Figures 3 and 4 show scanning electron micrographs of the planar and transverse views of a metallic W deposit obtained at 25 mJ/cm^2 on GaAs. Figure 3 shows the relatively smooth, granular microstructure of the film, with grains having an average size of 200–500 nm. Figure 4 shows the dense, regular columnar structure that is typical of good quality W layers. However, many films delaminated during or immediately after deposition. This adhesion problem was reduced by *in situ* heating of the substrates to 550 °C under vacuum prior to deposition. W films with thicknesses up to 2 μm were thus deposited without delaminating, and passed the Scotch tape test.

Krans[16] has reported that several cleaning cycles of GaAs with ''fresh'' solvents before deposition improved the adhesion properties of the W laser deposited films on GaAs. This can be understood in terms of our observations[17,23] that GaF_3 is formed upon exposure of GaAs to WF_6. The rate of this reaction is dependent upon the cleanliness of the GaAs samples, and is minimized by removing the oxides from the sample surface.[17] *In situ* heat treatment of the samples before W deposition also removes some of the native oxides, thus reducing the amount of GaF_3 formed at the interface and improving the adhesion of the W films.

C. Characterization of the W films

Figure 5 shows the Auger depth profile of a W film deposited at 25 mJ/cm^2 on GaAs. No F, C, or O was detected

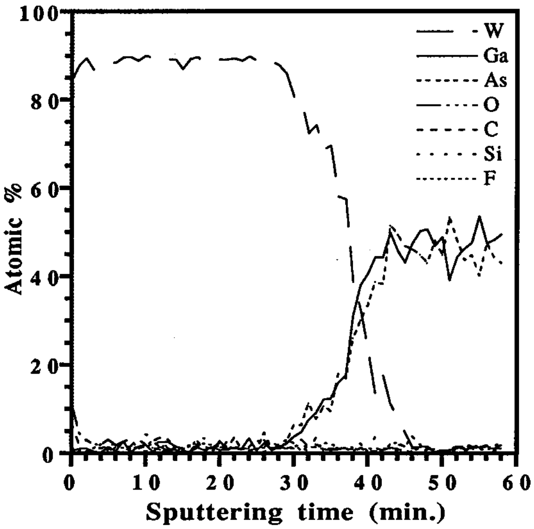

FIG. 5. AES depth profile of a W deposit on GaAs.

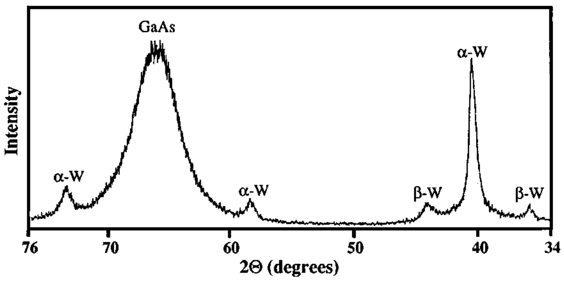

FIG. 6. XRD spectrum of a W deposit on GaAs.

in the bulk of the film or at the metal–semiconductor interface at concentrations above the noise level (1 at. %). This result is typical of deposition processes using WF_6, since this precursor is known to yield high purity W layers. Si was also not detected in the films. As noted earlier, SiH_4 plays a role in the reduction of WF_6, but the Si atoms probably evaporate through the formation of volatile silicon fluorides.[22] The interdiffusion between the W and the GaAs, is very small. No preferential As outdiffusion in the W is detected, indicating that there is a relatively sharp interface. This compares favorably with rapid thermal CVD,[24] Ar^+ laser[17] or even KrF excimer laser[25] deposited films using WF_6 and H_2, in which As is seen to diffuse into the metal. This is probably a consequence of the brief excimer laser induced heating of the substrate (of the order of 100 °C at 25 mJ/cm^2), along with the relatively low laser energy density needed to form metallic W from the WF_6/SiH_4 mixture. The combination of these two phenomena leads to a deposition process in which little, if any, damage is induced on the GaAs substrate.

The crystalline structure of the laser deposited W was determined by x-ray diffraction (XRD) spectroscopy. A representative XRD spectrum is shown in Fig. 6. The most intense peak, at 40.6°, is attributed to the α phase of W, and the two much weaker signals at 35.8° and 44.1° are attributed to the β phase of W. Clearly the majority of the deposited W are in the α phase, which is the low resistivity ($\rho_{\text{bulk}}=5.6\ \mu\Omega$ cm) stable (bcc) phase of pure W. In contrast, the β phase is metastable and is stabilized by the presence of some impurities such as F or O. The resistivity of the β phase can be up to 100 times higher than that of the α phase, and thermal anneals (>300 °C) are necessary to convert β phase W into the α phase.

Using a four-point probe method, a resistivity of 21 $\mu\Omega$ cm was measured for 0.5-μm-thick W films deposited at 25 mJ/cm^2. This value is nearly four times that of bulk α-W. It is lower than what was obtained by rapid thermal CVD[24] and comparable to the resistivity of plasma enhanced CVD[26] and laser CVD[15] W and confirms the purity and crystalline structure of the deposits as indicated by Auger depth profile and XRD measurements.

D. Fabrication and characterization of laser projected W Schottky diodes on GaAs

One of the advantages of using a laser based process in which few photochemical reactions are induced in the gas phase is the possibility of performing resistless single step patterning of a substrate by placing a mask in the path of the laser beam. Using this simple technique, we have studied the feasability of W projection patterning on GaAs. Using an optical system that was not optimized for this application, we deposited W patterns 60 μm wide and 1 μm thick. No deposit was formed on the nonirradiated area of the substrate, confirming that the dominant processes leading to the deposition of W take place at the surface of the substrate. This is in contrast to the deposition of W from WF_6 using a ArF excimer laser,[16] where WF_6 dissociation is triggered in the gas phase by the laser beam.

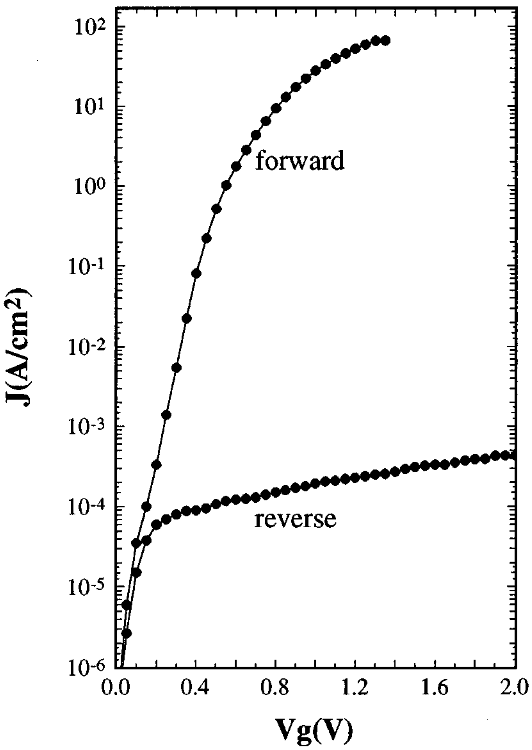

FIG. 7. $I-V$ curve of a typical W/GaAs Schottky diode fabricated by excimer laser projection patterning.

In order to determine the nature and the quality of the W/GaAs contact, we used samples having an ohmic contact on the back side of the GaAs wafer. AuGe (200 nm) and Ni (40 nm) layers were evaporated on the rough back side of the Si-doped GaAs. These samples were annealed under vacuum for 30 min at 550 °C, and formed AuGe/Ni/GaAs ohmic contacts. The substrates were then transfered under vacuum to the deposition cell and 200–300 μm sized W patterns were laser projected on the front side of the GaAs wafers. Figure 7 shows a typical $I-V$ curve of such a contact. Clearly the forward current is many orders of magnitude higher than the reverse current, indicating Schottky contact behavior. For several adjacent diodes deposited in a single step, the average barrier height and ideality factor obtained from such $I-V$ curves were 0.71 ± 0.05 and 1.2 ± 0.1 eV, respectively. The reverse current, however, is about 10^{-4} A/cm^2. This value is two orders of magnitude higher than what is expected for a diode with a barrier height of 0.71 eV. Such a high reverse current value is possibly due to leakage currents caused by the presence of some defects. The reverse characteristics and the ideality factor could probably be improved since these results are still nonoptimized. We believe that this is the first report of Schottky diodes fabricated by a resistless laser projection patterning technique.

IV. CONCLUSION

A KrF excimer laser beam incident normally incident on a GaAs surface was used to induce W deposition using a gas mixture containing WF_6 and SiH_4. Pure and uniform W films, having a resistivity of 21 $\mu\Omega$ cm, were thus obtained at laser fluences as low as 25 mJ/cm^2. Laser direct-projection patterning of 60 μm metallic W features on GaAs was also performed using a nonoptimized and basic optical system. $I-V$ measurements show that the W–GaAs structures thus formed are good quality Schottky diodes with an average barrier height of 0.71 eV and an average ideality factor of 1.2. To our knowledge, this is the first report of Schottky diodes obtained by a resistless laser projection patterning system. Further work is necessary to study the thermal stability of the diodes with annealing cycles up to 850 °C, as is required for SAG-MESFET fabrication, and to optimize the process in order to obtain micron or submicron features using this technique.

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