Excimer Laser-Induced Metallization for Si and GaAs Microelectronics

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ABSTRACT

We have investigated both the large area excimer laser-induced deposition of W and its silicides on GaAs to form thermally stable Schottky contacts, and the reduction of Cu(I) and Cu(II) compounds for the deposition of Cu interconnects for Si microelectronics. Using a KrF excimer laser at 25 mJ/cm^2 and a mixture of WF_6, SiH_4 and Ar, metallic W is deposited with an average growth rate of 1 Å/pulse. For Cu deposition, the precursor Cu(hfac)(TMVS) gives much purer deposits than the Cu(II) compounds which have been studied. For both processes, possible deposition mechanisms are discussed in terms of gas phase and surface reactions.

1. INTRODUCTION

The evolution of microelectronics technology presents major challenges in manufacturing processing, creating the need for ultra-clean technology and infrastructure[1,2,3,4]. All-dry processing solves some major manufacturing problems by simplifying costly air handling and clean room issues, as well as by eliminating a major source of particles and metallic contamination on wafers. Due to the increasing cost of large ultra-clean facilities, *in situ* processes performed in all-dry vacuum integrated chambers, or cluster tools, must be developed to avoid particle contamination.

Among the various cluster tools which need to be developed are high resolution all-dry lithography or direct patterning. The expected resolution limit of excimer laser optical lithography is 0.12 μm[5,6,7]. Not only can excimer lasers be used for deep UV lithography; they also offer the possibility of achieving one-step projection patterning of submicron features, under appropriate conditions. Indeed, UV photons are sufficiently energetic to induce surface chemical reactions, producing local thin film deposition or etch. This usually involves exposing the surface to an appropriate gas mixture. Single step excimer laser projection patterning is clearly compatible with *in situ* processing. Excimer lasers have been used for etching Si and GaAs[8], for doping Si and GaAs[9], as well as for thin film deposition on various substrates[10].

One of the key steps in microelectronic fabrication is metallization. We present here some recent results on the development of excimer laser-induced metallization for Si and GaAs microelectronics. More specifically, we have performed Laser-Chemical Vapor Deposition (LCVD) of W and its silicides on GaAs to form thermally stable Schottky contacts. In addition, we have investigated the reduction of Cu (II) and Cu (I) compounds for the deposition of Cu interconnects on SiO_2, Si_3N_4 and TiN. We focus on the deposition mechanisms over large areas and on the determination of the nature and the composition of the gases which will produce high quality metallization. High resolution patterning will require further development and will be presented in subsequent papers.

2. SYSTEM FOR EXCIMER LASER-INDUCED METALLIZATION

Figure 1 schematically shows the system for large area excimer laser-induced metallization. Two deposition chambers were developed, one for each metal to be deposited. In each case, the substrate is placed in a high vacuum stainless steel cell having a base pressure less than 10^{-6} Torr. A gas distribution system is connected to the chamber and contains the metal precursor gas, reducing gases, and Ar as a buffer and purging gas. The slightly focused laser beam from the KrF excimer laser (248 nm), pulsed at a few Hz, passes through a quartz window and is incident perpendicular to the substrate. The system is connected to a

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vacuum transfer module by which the samples may be transferred to an X-ray photoelectron spectrometer (XPS) in order to study the reactions taking place at the surface of the samples as well as the composition of the deposits. A mass spectrometer may also be used to investigate the various chemical species present in the chamber.

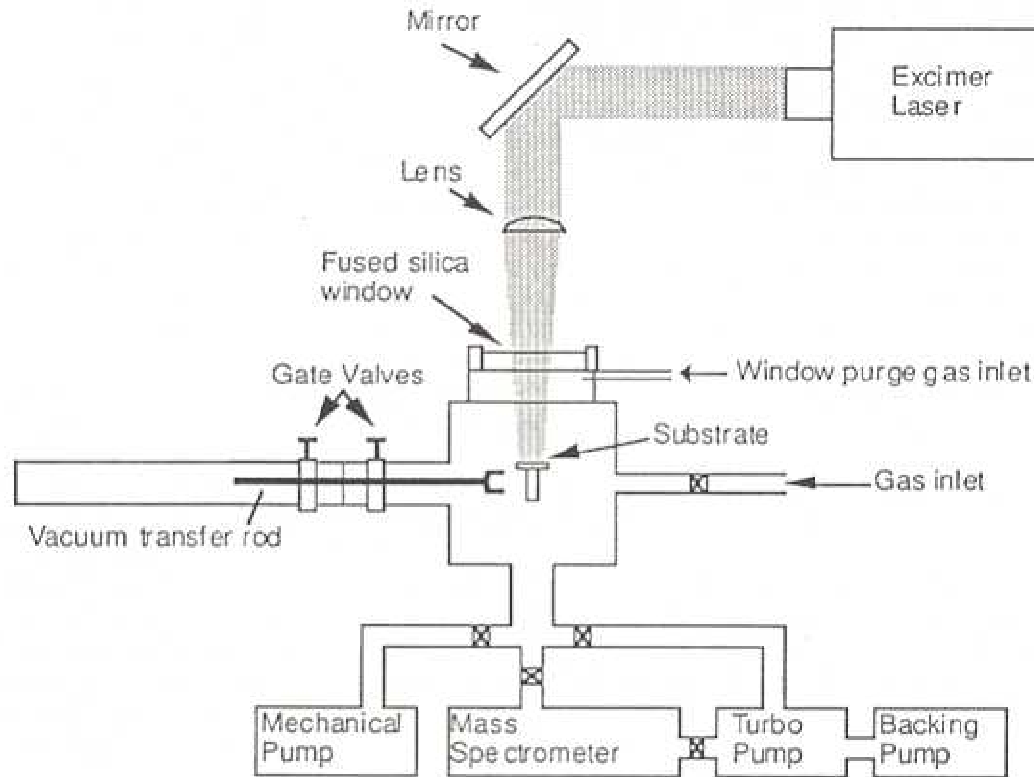

Figure 1: System for excimer laser-induced metallization

3. EXCIMER LASER-INDUCED DEPOSITION OF W ON GaAs

The development of in-situ processes 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[11]. Excimer laser-induced Cl_2 etching of GaAs and *in situ* doping have recently been achieved[8]. However, gate metallization for GaAs transistors continues to be a problem. Tungsten[12] and its silicides[13] have been used for self-aligned gates. These materials have previously been deposited on GaAs using various techniques, such as magnetron sputtering[14], plasma-enhanced CVD[15], rapid thermal CVD[16] and large area ArF excimer laser CVD with the beam parallel to the substrate[17]. However, none of these techniques can be incorporated in a resistless *in situ* photo-process. We have therefore investigated the possibility of W and WSi_x deposition on GaAs by projection patterning using a KrF excimer laser CVD process.

In our system, the metal precursor is WF_6, while SiH_4 and H_2 are used as reducing gases. The substrates were (100) oriented undoped and Si-doped (10^{17} cm^{-3}) liquid encapsulated Czochralski GaAs wafers. They were cleaned using a series of solvents, dipped into a hot 1:1 HCl: H_2O solution and dried in flowing nitrogen before being introduced into the deposition chamber. Typical operating pressures were 40 Torr when H_2, Ar and WF_6 were used, and 14 Torr when SiH_4 was used instead of H_2. Lower pressure was used in the latter case in order to minimize the reaction between SiH_4 and WF_6 in the gas phase[18].

We have already shown evidence of a reaction between WF_6 and GaAs with and without KrF laser irradiation[19,20]. GaF_3 formation and a loss of As (probably through the formation of volatile arsenic fluorides) were detected at the surface of our samples. Metallic tungsten was also deposited through the H_2 reduction of WF_6 for laser fluences of around 67 mJ/cm^2. However, to be able to obtain sustained growth of the W layer on GaAs, a laser-induced temperature rise of about 400°C was needed. At such temperatures, WF_6 and GaAs become very reactive, and Dektak profilometer measurements show surfaces with

trenches and hillocks formed on the areas irradiated by the laser. These observations are similar to those of Lecours et al[21], when an Ar^+ laser emitting at 514 nm was used to deposit W on GaAs under conditions similar to ours. These authors detected such features on the substrate after exposure to a laser power of 75 mW, not enough to cause the thermal decomposition of GaAs. In some of our experiments, W deposits of up to 0.4 µm were obtained, but these proved to be non-reproducible.

To overcome the problem of the relatively high growth temperature, we have investigated the use of SiH_4 instead of H_2 as the reducing gas. W can be deposited using a WF_6:SiH_4 mixture at temperatures as low as 175°C[22]. Therefore, laser fluences lower than those needed to induce W deposition with H_2 can be used to dissociate WF_6 into W through the SiH_4 reduction reaction. The reaction between WF_6 and GaAs can then be limited at such low fluences. Furthermore, neither WF_6 nor SiH_4 absorb the 248 nm photons of the KrF excimer laser in the gas-phase. This is a necessary criterion for the performance of projection patterning. However, the adsorbates of these two species on the surface may have electronic spectra which are quite different from their gas phase configurations, so that some photochemistry could be obtained at the substrate surface.

The most uniform and reproducible deposits were obtained at laser fluences of about 25 mJ/cm^2. Figure 2 shows the W 4f XPS spectrum of a deposit obtained, under the conditions described above, after 3000 pulses, using a gas mixture of 1sccm WF_6, 3 sccm SiH_4 and 80 sccm Ar. Note that this sample was transferred to the analysis chamber under vacuum, in order to avoid oxidation of the W deposit. The presence of W 4f peaks at -31.5 eV and -33.6 eV is an evidence that the W on the substrate is indeed metallic. After 5000 pulses, a deposit of about 0.5 µm was obtained, giving an average deposition rate of about 1 Å per pulse. However, since it takes about 2000 pulses to nucleate the film on GaAs, the deposition rate per pulse is actually higher than this value.

A rough calculation of the temperature increase due to an 8 ns, 25 mJ/cm^2 KrF excimer laser pulse gives a value of about 180°C. Since the substrate was at room temperature before laser irradiation, we can estimate a deposition temperature of about 200°C. This is in good agreement with previous reports of W deposition from a mixture of WF_6 and SiH_4[23]. At laser fluences much higher than 25 mJ/cm^2 (~ 50 mJ/cm^2), the uniformity and smoothness of the deposits degrade and islands as high as 5 µm are formed. Moreover, at such high laser fluences we have detected the formation of powder-like particles on the substrate. This powder is the result of a gas-phase reaction between WF_6 and SiH_4 which may occur when the substrate temperature becomes too high and heats the surrounding gas[23]. At lower laser fluences (10 mJ/cm^2), the growth rate becomes very small, but this range still needs to be investigated in more detail. This is especially so, as any photochemical effect, if present, can be detected at very low fluences.

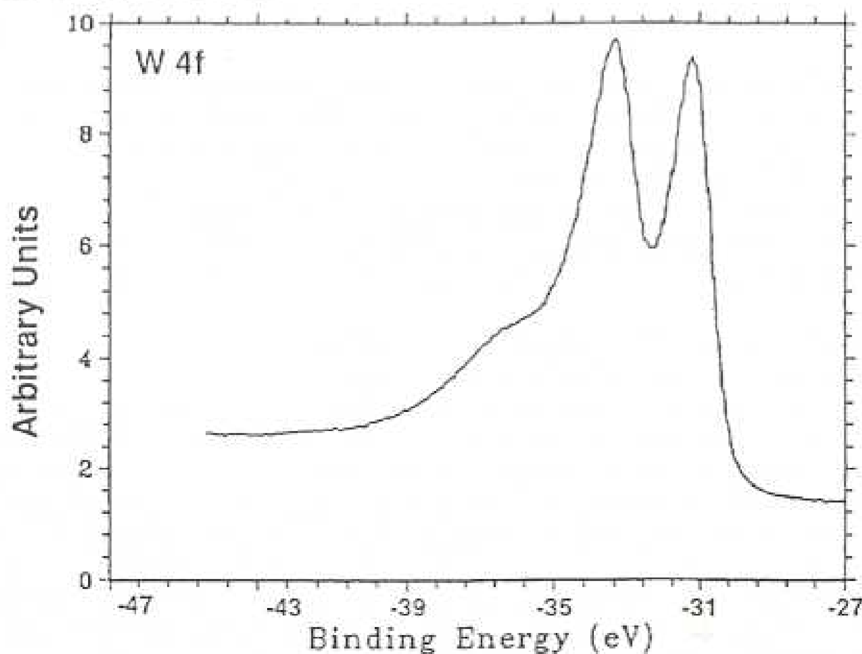

Figure 2: W 4f XPS spectrum of a deposit prepared from a WF_6/SiH_4 gas mixture.

It was also found that the deposition process is very dependent upon the reactive gas mixture in the cell. For example, if the above gas mixture is changed to 3 sccm of WF_6, 1 sccm of SiH_4, maintaining 80 sccm Ar buffer flow, there is no W deposition at 25 mJ/cm^2. This too is not very surprising since it is known that the initiation temperature of the SiH_4 reduction reaction depends strongly upon the composition of the gaseous ambient[24].

Our XPS analysis shows that, even when we use SiH_4, GaF_3 is formed on the surface of the GaAs substrate. However, since the laser fluences used are much lower than those used with H_2, the amount of GaF_3 formed is less when using SiH_4. This issue can have important consequences on the interface properties of the W-GaAs contact. Furthermore, the presence of stable, non-volatile GaF_3 on the surface of the substrate may explain the difficulty in nucleating a W seed layer on a GaAs surface, as noted by many authors[15,17,19], in a WF_6 based CVD process. The non-volatile fluoride at the substrate surface reduces the number of available nucleation sites for metallic W formation. Therefore, reducing the amount of GaF_3 makes the W layer nucleation easier, in the abscence of any gas-phase reaction, and it has important consequences on the surface mechanisms of the growth of the metallic layer.

4. EXCIMER LASER-INDUCED DEPOSITION OF COPPER FOR Si MICROELECTRONICS

Copper is another attractive material for future microelectronics applications, as it combines low resistivity and high electromigration resistance. These properties make it a serious prospect for the fabrication of upper level interconnect lines in ULSI (smaller than 0.25 μm) devices. The aluminum alloys currently used heat up and form open circuits at these dimensions. However, dry and wet etching of copper with micron and sub-micron resolution is difficult at best, raising the need for a selective deposition process, such as excimer laser-chemical vapor deposition. This technique has the double advantage of being a low temperature process and of permitting high resolution projection patterning of interconnects by exposing the substrate to the laser through a mask.

We have investigated the excimer laser deposition of copper on various substrates. Since no copper-containing precursor is gaseous at room temperature, solid and liquid organometallic compounds were heated to obtain sufficient vapor pressure. We studied the deposition of copper via two different solid copper (II) compounds, $Cu(hexafluoroacetylacetonate)_2$ (or $Cu(hfac)_2$), and $Cu(hexamethylacetylacetonate)_2$ (or $Cu(hmac)_2$), and one liquid copper (I) compound, Cu(hfac)(trimethylvinylsilane) (or Cu(hfac)(TMVS)).

4.1 Cu(II) precursors

With $Cu(hfac)_2$, heated to 65°C, depositions on two insulating substrates, Si_3N_4 and SiO_2, were carried out with laser wavelengths of either 193 nm or 248 nm. With $Cu(hmac)_2$, heated to 80°C, deposits were obtained on SiO_2 using a wavelength of 248 nm. The vapors of the precursors were carried to the reaction chamber by 2080 sccm of H_2, which also acted as a reducing agent. Typical pressures in the chamber during deposition were 2-10 Torr. Up to 10000 pulses were delivered to the substrate at a repetition rate of 10 Hz. It should be noted that all experiments with those two precursors were done with a deposition system equipped only with a mechanical rotary pump, giving a base pressure in the reaction chamber of 10^{-3} Torr. No vacuum transfer module was available at the time so the samples were transfered in air to the X-ray photoelectron spectrometer.

Deposits were studied using XPS and were always found to be strongly contaminated with carbon. C/Cu ratios of 13 for $Cu(hmac)_2$ and 8 for $Cu(hfac)_2$ were common, even under the best experimental conditions. Reduction of the copper to its metallic state was not complete in either case. Oxygen and fluorine were also present in large concentrations, but those elements are believed to be primarily surface contaminants. The deposits were too thin and discontinuous to permit sputtering of these surface contaminants. A possible explanation of this strong contamination, as suggested by Houle and coworkers[25], is that the reduction of the precursor occurs mostly through a photolytic process, which leads to the formation of non-volatile carbon-containing species by breaking up the hfac (or hmac) ligand. Therefore, a precursor which contained less of these ligands would be expected to lead to deposits with less contamination.

The precursor $Cu(hmac)_2$ was also found to react with the SiO_2 substrate when exposed to the excimer laser, forming silicon carbide. Stoechiometry, as determined by evaluating the area of the carbon and silicon peaks in the XPS spectra, was found to be very close to 1:1 (atomic C:Si). Obviously, such a reaction between substrate and precursor should also be avoided, especially if copper is to be deposited on vias connecting to lower level interconnects, since it would drastically increase contact resistivity.

4.2 Cu(I) precursor

All other reports of UV-induced CVD of copper using copper (II) precursors, using either mercury arc lamps[25,26], pulsed excimer lasers[25,26,27] or cw frequency-doubled Ar^+ lasers[25,26] indicated that considerable carbon contamination is present in the deposits. Introduction of an alcohol as coreductant in the reaction chamber has been shown to increase the purity of the deposits, but not to acceptable levels[25]. New copper (I) compounds have recently been introduced and shown to produce pure copper films in conventional, thermal CVD[28], without the need for a reducing gas.

The excimer laser-induced CVD of copper using such a copper (I) precursor, Cu(hfac)(TMVS), has been studied. For these experiments, a high vacuum deposition system, similar to the one used for W deposition, was assembled. It is composed of a turbo-molecular pump, a mass spectrometer and a magnetically coupled vacuum transfer module. This liquid compound, also known as CupraSelect™, was obtained from Schumacher Company. It was heated to 45°C, where its vapor pressure is approximately 1 Torr, and mixed with a carrier gas of 15 sccm of Ar, yielding a typical total pressure of 4 Torr in the reaction chamber. Substrates were silicon covered with a TiN thin film (800 Å) and were heated, as was the reaction chamber, to 60°C. TiN was chosen since it is a good copper diffusion barrier and is commonly used in microelectronic fabrication processes. The substrates were exposed to the precursor and typically irradiated with 3000 pulses of the KrF line of an excimer laser (248 nm). The formation of deposits on the quartz window was unavoidable with our present deposition system. While a purge gas system was being designed, UV-transparent quartz substrates were fixed on the inside of the window to permit analysis of these deposits. Films were formed both on TiN and quartz, although the latter were much thicker producing a thick filter, preventing the exposure of the TiN substrate to sufficient energy for an adequate number of pulses. The energy density at the surface of the TiN substrate originally was of the order of 5 mJ/cm^2 at the beginning of the experiments. This value decreased as the filter forming on the quartz substrate grew thicker.

XPS of the deposits on the quartz substrate showed that Cu was reduced to its metallic state. Figure 3 shows that, although present as surface contaminants, fluorine and oxygen are not present in the bulk of the films, and that the C/Cu atomic ratio is five times lower in the bulk of the deposit than on the surface, reaching 0.8 in the sputter-cleaned samples. Profilometry measurements were also performed. Deposits on quartz samples which had been exposed to 2500 pulses were 0.1 µm thick.

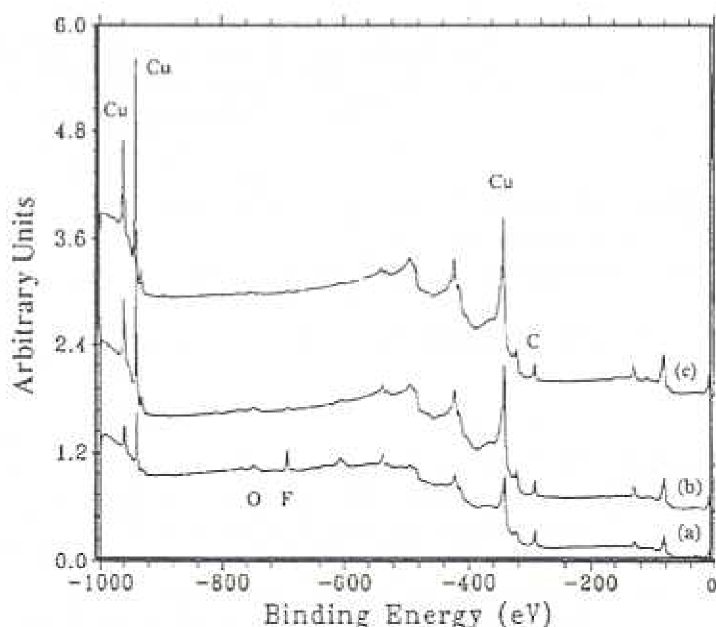

Figure 3: XPS survey of deposited Cu film on quartz: (a) as deposited, (b) after argon sputtering for 70 s. at 2 KV, and (c) after sputtering for 280 s.

Deposits on the TiN substrates showed comparable levels of surface contamination under XPS analysis, but were too thin to permit sputtering. Deposits were uniform, with grain size, evaluated from scanning electron microscopy (SEM) and atomic force microscopy (AFM) measurements, ranging from 200 to 400 Å. They also showed very good adhesion, as they passed the adhesive tape test.

Although Cu(hfac)(TMVS) in excimer laser induced CVD has led to much purer deposits than Cu (II) precursors, still more work is needed to make this process viable. Deposits on the window should be eliminated, and the carbon concentration has to be further reduced. It is expected that the use of an alcohol as a coreductant with Cu (I) compounds could produce purer deposits, as is the case with Cu (II) precursors.

5. CONCLUSION

In response to the importance of all-dry patterning for *in situ* processing, we have investigated excimer laser-induced metallization for Si and GaAs microelectronics. We have shown that excimer lasers can induce the deposition of metallic W and its silicides from WF_6 and SiH_4 on GaAs. Investigation of excimer laser-induced deposition of Cu from Cu(hfac)(TMVS) has been presented. More work has to be done on both processes in order to determine the optimum conditions for producing high quality metals in a reproducible manner. Then, based on our large area process conditions, image projection mode will be investigated to obtain high resolution patterns. This will be the subject of subsequent work.

6. ACKNOWLEDGMENTS

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