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Excimer laser-induced metallization for in situ processing on Si and GaAs

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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 a Cu(I) compound 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 reduction by H_2 of the precursor Cu(hfac)(TMVS) under a KrF excimer laser illumination of 9 mJ/cm^2 gives metallic Cu with a Cu/C ratio of 4.35. For both processes, possible deposition mechanisms are discussed in terms of gas phase and surface reactions.

1. Introduction

The development of in situ processes performed in all-dry vacuum integrated chambers (cluster tools) could solve some major manufacturing problems related to particle contamination, costly air handling and clean room systems [1–4]. The use of excimer lasers is particularly suitable for such processes since they can be used to perform one-step projection patterning of submicron features. Under the appropriate conditions, the excimer laser UV photons can induce surface chemical reactions to achieve etching [5], doping [6], and deposition [7].

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 a Cu(I) compound for the deposition of Cu interconnects on SiO_2 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.

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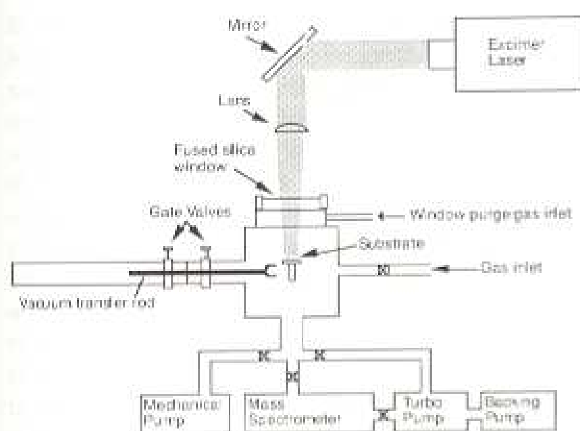

Fig. 1. System for excimer laser-induced metallization.

2. System for excimer laser-induced metallization

Fig. 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 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.

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 [8]. Excimer laser-induced Cl_2 etching of GaAs and in situ doping have recently been achieved [5]. However, gate metallization for GaAs transistors continues to be a problem. Tungsten [9] and its silicides [10] have been used for self-aligned gates. These materials have previously been deposited on GaAs using various techniques, such as magnetron sputtering [11], plasma-enhanced CVD [12], rapid thermal CVD [13] and large area ArF excimer laser CVD with the beam parallel to the substrate [14]. 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 were 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 [15]. We have already shown evidence of a reaction between WF_6 and GaAs with and without KrF laser irradiation [16,17]. 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. [18], 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 [19]. 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. Fig. 2 shows the W 4f XPS spectrum of a deposit obtained, under the conditions described above, after 3000 pulses, using a gas mixture of 1 sccm 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

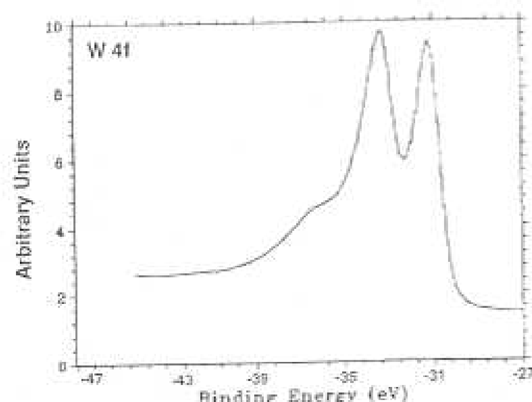

Fig. 2. W 4f XPS spectrum of a deposit prepared from a WF_6/SiH_4 gas mixture.

oxidation of the W deposit. The presence of W 4f peaks at −31.5 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 [20]. 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 [20]. 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.

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 [21].

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 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 [12,14,16], 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 Cu on TiN and SiO_2

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 already studied the deposition of copper via some solid copper (II) compounds [22] and found as in other UV-induced CVD processes [23,24] that deposits were always strongly contaminated with carbon. A possible solution to this problem is to use new copper (I) compounds which have recently been introduced and shown to produce pure copper films in conventional, thermal CVD [25], without the need for a reducing gas. Such a copper (I) precursor has been used by Han et al. [26] in their pyrolitic Ar^+ laser direct writing system to produce high quality copper lines.

The excimer laser-induced CVD of copper using Cu(hfac)(trimethylvinylsilane) (or Cu(hfac)(TMVS)) has been studied. This copper (I) compound, also known as CupraSelect™, was obtained from Schumacher Company. Since Cu(hfac)(TMVS) is liquid at room temperature, it is placed in a bubbler and heated to 45°C, giving a vapor pressure of about 1 Torr. The rest of the piping, as well as the reactor, are heated to 60°C to avoid condensation. The precursor is carried to the deposition chamber by Ar or H_2. To avoid any deposition on the window, it is purged with an Ar flow before and during laser exposure.

Cu was deposited on TiN (80 nm) on Si, and SiO_2 (600 nm) on Si. TiN was used as it is a good barrier layer, preventing copper diffusion into Si. SiO_2 was used for resistivity measurements, as well as to study the deposition selectivity on different substrates. Samples were degreased then dried at 115°C for 30 min before experiments. The reaction chamber was pumped to a base pressure of 10^{-7} Torr. The deposition was done at a laser repetition rate of 20 Hz. The laser beam was unfocused or slightly focused, giving energy densities ranging from 9 to 51 mJ/cm^2 at the substrate. The number of pulses was varied from 1000 to 20000. In addition to 15 sccm of Ar purge gas at the window, 28 sccm of Ar or H_2 carrier gas was used, giving total pressures in the reaction chamber of 6.0 and 5.5 Torr, respectively.

The thickness of the copper films was measured with a Dektak profilometer, and was studied as a function of both the number of laser pulses and the energy density incident on the substrate. Fig. 3 shows the variation of the film thickness with the number of pulses, using Ar as the carrier gas, and at an average energy density of 51 mJ/cm^2. These thicknesses were measured at the center of the deposits, where the energy density is the largest. It can clearly be seen that two growth regimes are obtained: until about 4000 pulses, the film grows at an average rate of 0.15 Å/pulse, while for a higher number of pulses, this rate goes up to 0.70 Å/pulse. For a laser repetition rate of 20 Hz, these values correspond to 3 and 14 Å/s, respectively. This transition between two deposition rates was seen to occur

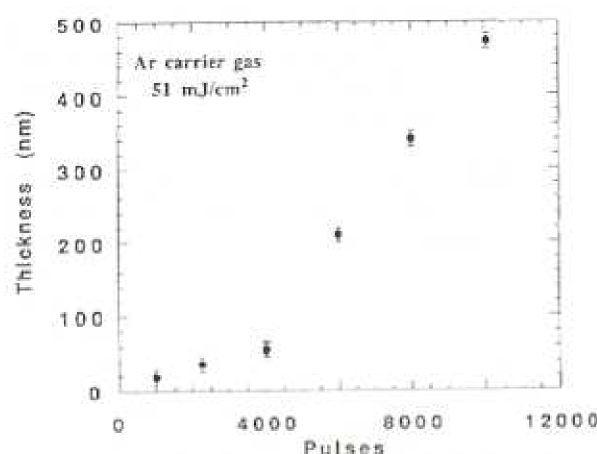

Fig. 3. Cu thickness of films made at 51 mJ/cm² in Ar as a function of the number of excimer laser pulses.

at the various energy densities studied, but could not be related to a particular thickness or number of pulses. For instance, at an energy density of 18 mJ/cm², the transition was observed after about 10000 laser pulses. Furthermore, the films grown at low energy densities, without focusing the laser beam, have a very uniform thickness compared to the ones grown with a high fluence, focused laser beam, for which thickness varies significantly along the diameter of the deposits. it should also be noted that the use of hydrogen appeared to enhance the growth rate, but a more complete study should be performed to quantify this phenomenon.

Fig. 4 shows the Cu $2p_{3/2}$ spectra of various as-deposited films. The binding energy position of the main peak and its small full width at half maximum are indicative of metallic copper. We therefore conclude that complete reduction of Cu(hfac)(TMVS) was achieved. However, large quantities of carbon, oxygen and fluorine were also detected at the surface. These elements originate from unreacted and/or partly-reacted reduction products still adsorbed on the surface after laser exposure. No silicon was detected, indicating the absence of TMVS on the surface. This was expected, since a rapid dissociative desorption of the TMVS ligand is observed upon the adsorption of Cu(hfac)(TMVS), even at low temperatures [27]. When high energy densities

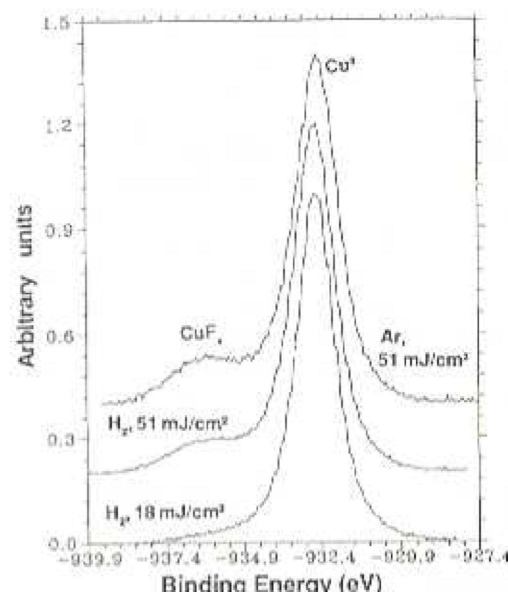

Fig. 4. Cu $2p_{3/2}$ spectra for various deposits made at 18 or 5 mJ/cm², with and without H_2.

are used, some copper at the surface is bonded t fluorine. This is indicated by the presence of secondary peak at higher binding energy, which i what we expect, since fluorine is more electroneg ative than copper. We note that the use of hydro gen as the carrier gas, and more importantly th lowering of the energy density, inhibit the forma tion of this copper fluoride. The rest of th fluorine present at the surface was found to b bonded to carbon, forming various CF_x. Carbo was detected under various forms, consisting o CF_x, CO and C.

After sputtering of the samples with Ar^+ (keV, slightly focused ion beam), it was found tha most of the impurities are only present at th surface. In the bulk, oxygen is not detected, whil fluorine and carbon concentrations are reduce

Table 1
Atomic ratios for various Cu films deposited by excimer lase induced decomposition of Cu(hfac)(TMVS)

Sputtered samples	Cu/C	Cu/F
Ar, 51 mJ/cm², 10000 pulses	1.69	3.57
H_2, 51 mJ/cm², 10000 pulses	2.17	3.57
H_2, 9 mJ/cm², 15000 pulses	4.35	15.0

by a factor of ten compared with their surface values. Table 1 lists the various atomic ratios evaluated from analysis of the XPS spectra. Those results were also supported by AES profiling. Using hydrogen and operating in the low growth rate regime result in films with less carbon and fluorine incorporation. Although the impurity levels are still non-negligible, the obtained ratios represent an extremely significant improvement when compared to previous results of excimer laser-induced CVD of copper, using Cu(II) precursors [22,23].

Preliminary four-point and two-point probe resistivity measurements were performed on films deposited on SiO_2 and a resistivity of 41 $\mu\Omega \cdot cm$ was obtained. The most conductive deposits, made at low energy densities, were also relatively thin because of the low growth rate. Therefore, good conductive contact was hard to establish during measurements and our results probably include high contact resistance effects. Therefore, the actual resistivity of the film is expected to be smaller than the measured value. To our knowledge, this is the first reported resistivity value for an excimer laser-induced CVD grown copper film. Further measurements, with thicker deposits, are currently under way.

An adhesive tape test was also performed on most deposits, and all films on TiN were found to adhere well to the substrate. Only a very thin removal of some of the rougher regions was observed in some cases. The rougher regions of the films grown on SiO_2, however, did not adhere well and were easily stripped off, leaving behind a smoother surface.

In laser-induced CVD, the identification of the mechanism responsible for the deposition is always problematic when the beam is incident on the substrate (perpendicular geometry). Deposition can be induced either (i) photolytically, with the photons directly breaking bonds of the precursor molecule adsorbed on the substrate surface or in the gas phase, or (ii) pyrolytically, with the substrate heating up under laser exposure. Both processes can be (and often are) present at the same time. In the work of Han et al. [26] where a visible wavelength laser is used, the decomposition mechanism is clearly pyrolitic, thus leading to high quality Cu films, as in the conventional thermal CVD process. However, in our case, although photothermal mechanisms cannot be ruled out, since the estimated temperature rise induced in TiN by the laser could be sufficient for thermal CVD to occur, there are two strong indications that photolytic processes are taking place. First, the fact that deposits were grown on the quartz window, when performing experiments without any purge gas, strongly indicates photolytical decomposition, since the window is UV transparent and therefore cannot heat up under excimer laser exposure. Second, a rough evaluation of the temperature rise of TiN and that of copper under our laser exposure conditions shows that TiN reaches a higher temperature, due to its lower thermal conductivity. Therefore, if the reaction was entirely pyrolytic, it would be expected that the growth rate when depositing directly on TiN (i.e., for the first few thousand laser pulses) would be higher than the growth rate when depositing on a pre-existing copper film (i.e., for the next few thousand laser pulses). However, it may be seen from Fig. 3 that this is not the case; the high growth rate regime occurs after a certain thickness of copper is already deposited. A photolytic process must then be occurring, which could be responsible for the impurity incorporation. The relative importance of the two mechanisms and their effects on the film purity cannot yet be determined, but further experimentation, using very low energy densities are under way. Under these conditions, the temperature rise of the substrate will not be sufficient to induce the thermal CVD of Cu(hfac)(TMVS), which occurs at temperatures as low as 120°C [28].

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 on TiN and SiO_2 of metallic 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, the image projection mode will be investigated to obtain high resolution patterns. This will be the subject of subsequent work.

Acknowledgments

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