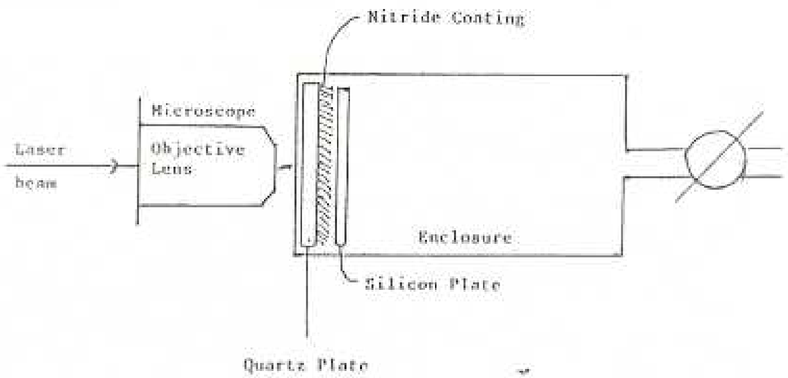

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LASER-ASSISTED LOW TEMPERATURE DEPOSITION OF WSi_x FROM WF_6 AND SiH_4

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ABSTRACT

A laser direct writing system has been developed for low temperature deposition of WSi_x on TiN from a gas mixture of WF_6 and SiH_4. An Ar^+ laser (488 nm, 1.5 W) and a diode laser (796 nm, 1.0 W) are used as photon sources. Lines are written at scan speeds of up to 100 µm/s from a flowing gas mixture of WF_6 and SiH_4 diluted in Ar. Lines 1.5 to 11 µm wide and 20 to 180 nm thick are obtained at a writing speed of 100 µm/s with the Ar^+ laser. Lines written using the diode laser are typically 4 to 12 µm wide and 160 to 860 nm thick. W/Si ratio in the deposits, as measured by Auger electron spectroscopy (AES), is between 1.5 and 1.8.

Surface analysis of the interaction of this gas mixture with the TiN surface without laser irradiation shows that W, Si and F are adsorbed on the surface when exposed simultaneously to WF_6 and SiH_4 producing an adsorbed layer where W/Si ratio is 1.3 and F/W ratio 1.7.

INTRODUCTION

The modification of microelectronics circuits is one of the principal applications of laser direct writing [1,2]. Since those modifications are performed on completed circuits, low temperature processing is necessary in order to prevent heat damage to the underlayer structures.The laser-assisted deposition of W from WF_6 and SiH_4 has been reported to proceed at temperatures as low as 175 °C [3].

Even though laser-deposition of various metals and metal silicides have been studied in recent years and many potential applications have been demonstrated in research laboratories [4,5], it is difficult to introduce such systems in the manufacturing environment [6]. In general, the lasers used in those processes are large and expensive. Maintenance and reliability are also important issues for industry. For this reason, we developed a reliable, compact and relatively low cost deposition system based on a diode laser. We investigated low temperature laser assisted deposition of WSi_x from WF_6 and SiH_4 and compare the results obtained with this system to those obtained with a conventional direct writing system based on an Ar^+ laser. As the deposition from this gas mixture greatly depends on the surface processes [7], we studied the gas surface interaction without laser irradiation by X-ray photoelectron spectroscopy (XPS).

LASER DIRECT WRITING SYSTEM AND EXPERIMENTAL PROCEDURE

The laser direct writing system has been presented elsewhere [8]. In this system the laser acts as a heat source to initiate a pyrolitic process. Two types of lasers were used. First, the beam of an Ar^+ laser (488 nm, 1.5 W) is focalized on the substrate to a 2 µm circular spot, using a long working distance 25 X, 0.31 NA objective. The lines deposited with this conventional system are compared with those deposited with the newly developed system which uses an AlGaAs diode

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laser array emitting at λ=796 nm with a maximum power of 1 W. The diode laser beam divergence is 10° and 40° in the two directions transverse to the propagation. This laser beam is collimated with a 0.5 NA objective and the ellipticity is reduced with a 4:1 anamorphic prism pair. The collimated and shaped beam is then focused on the substrate using the 0.31 NA focalization objective. In this case, the spot at the substrate is elliptic with axes of 12 and 93 µm at 1/e intensity. The optical system efficiency is 58 %, which yields 580 mW at the substrate.

Substrates are 100 nm thick reactively sputtered TiN films on 800 nm SiO_2 films deposited on c-Si. Before deposition the samples are cleaned in hot TCE, acetone and propanol, rinsed in DI water and dried at 120 °C for 20 to 30 minutes. They are then placed in a stainless steel reaction chamber closed by a fused silica window and pumped to a base pressure of 10^{-2} to 10^{-3} Torr. Line formation is achieved by moving the reaction chamber using computer controlled stages having a 0.1 µm resolution. Lines are written at 100 µm/s, the maximum velocity of the system, in the direction parallel to the long axis with the diode laser and in any direction with the Ar^+ laser. The system can be operated in a static mode, where the cell is filled to the desired pressure and gas ratio before processing, or in a dynamic mode, where the gases are kept flowing at an established flow rate ratio. The reaction cell is kept at room temperature during the experiment.

GAS-SURFACE INTERACTION

Room temperature surface interaction between the gaseous precursors (WF_6 and SiH_4) and the TiN substrate are studied by XPS in order to determine the surface conditions before laser irradiation. XPS analyses were performed in a VG Escalab MKII system. The samples are first analyzed immediately after cleaning and a second analysis is performed after exposure to the reactive gases. The samples are moved under vacuum from the process chamber to the analysis chamber using a transfer module.

The clean TiN surface is oxidized after air exposure as previously reported [9]. We did not attempt to remove this oxide as laser deposition were performed under these conditions.

Exposures to reactive gases, WF_6 and SiH_4, individually or simultaneously were performed. There is no detectable reaction between SiH_4 and TiN after exposure to 1.5 sccm of SiH_4 (P=0.9 Torr) for 15 minutes. However, WF_6 adsorbs readily on the TiN surface after a 15 minutes exposure to 1.0 sccm of WF_6 (1.0 Torr). The F/W ratio in the adsorbed layer is 4.4, as estimated from F 1s and W 4d peaks. This result is comparable to those obtained on SiO_xN_y [10].

When the substrate is exposed alternatively, first to WF_6 then to SiH_4, W and F adsorbed on the surface are observed, as in the case of exposure to WF_6 alone, and no adsorption of Si is detected. This is different from the observations of Iwasaki et al. [11] at 450 °C where Si adsorption was observed. However, this is in accordance with those of Yu et al. [9] who find that the reaction of SiH_4 with oxidized TiN at 60°C is very weak.

When the sample is exposed to WF_6 and SiH_4 simultaneously, an adsorbed layer containing W, F and Si is formed. For 30 minutes exposure to 1 Torr of WF_6 and 3 torr of SiH_4 in a static reactor, the F/W ratio is 1.7 and the W/Si ratio is 1.3. These ratios show that there is a partial reduction of WF_6 by SiH_4 under these conditions. However, no metallic tungsten was observed.

LASER DIRECT WRITING OF WSi_x ON TiN

Some of the preliminary results of the diode laser direct writing of WSi_x on TiN in a static reactor have already been presented elsewhere [12]. In summary, lines 4 to 15 µm wide and 110 to 950 nm thick were deposited at 5 µm/s in a gas mixture of 1 Torr WF_6 and 3 Torr of SiH_4. The W/Si ratio in these deposits is between 1.1 and 1.4 as measured by Auger electron spectroscopy (AES). This gas mixture can be extremely reactive and often leads to uncontrolled deposition. A more controlled and reproducible deposition is obtained when the process occurs in a dynamic mode. Here, we focus on the dynamic mode deposition with the emphasis on comparing the deposition from both types of lasers (Ar^+ and diode).

We observed that the laser power, and hence the temperature, needed to initiate the reaction strongly depends on the gas mixture. Due to the beam characteristics of the laser diode (spot size and wavelength), the maximum temperature rise achievable is limited and deposition can only be performed in a narrow set of conditions. We then use gas mixtures of 1 sccm WF_6, 3 sccm SiH_4 and variable Ar flows for which the deposition occurs at low temperature.

Very uniform lines are deposited with this gas mixture using the laser diode [13,14]. In figure 1 we see the variation of the thickness as a function of laser power for two different Ar flows. Line thickness increases as power increases but decreases with increasing Ar flow. Lines are typically 150 to 800 nm thick and 4 to 12 µm wide. Using the spot dimension and the writing speed this gives average vertical growth rates ranging from 160 to 860 nm/s.

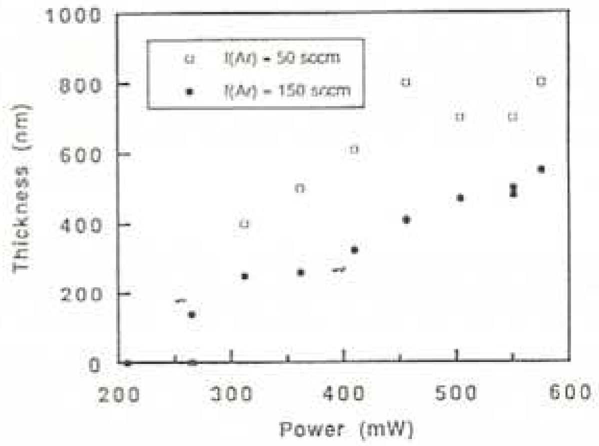

Figure 1. Thickness of WSi_x lines deposited on TiN with a diode laser as a function of laser power for two different Ar flows. $f(WF_6)$ = 1 sccm, $f(SiH_4)$ = 3 sccm. Total pressures are 8.9 and 16.2 Torr. Writing speed is 100 µm/s.

Figure 2 shows the line thickness as a function of laser power for lines deposited with the Ar^+ laser in the same gas conditions that those used with the diode laser. Line thickness now range from 20 to 180 nm and widths are from 1.5 to 11 µm. This gives growth rates ranging from 1 to 9 µm/s. We also see in figure 2 that, for low powers, the line thickness increases when the laser power increases as is the case of the laser diode. However, for high laser power, the thickness reaches a maximum then saturates. This maximum thickness depends on the Ar flow and decreases when the Ar flow increases.

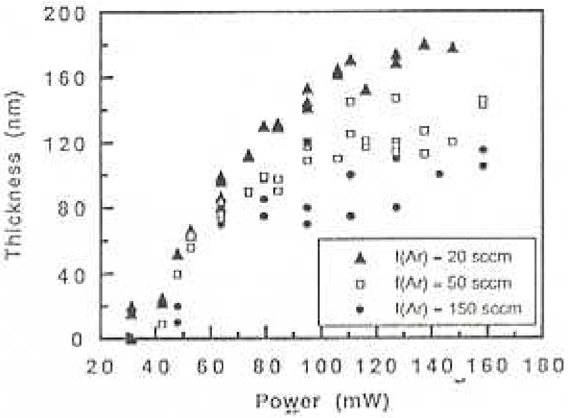

Figure 2. Thickness of lines deposited on TiN with an Ar⁺ laser as a function of power. f(WF$_6$) = 1 sccm, f(SiH$_4$) = 3 sccm,Total pressures are 5.6, 8.9 and 16.2 Torr. Writing speed is 100 µm/s.

The deposited lines composition was measured by AES. Within the limit of detection (1% at.) no fluorine is detected. Aside from surface contamination, attributed to atmosphere exposure between deposition and analysis, no carbon, nitrogen or oxygen are detected in the deposited film. The W/Si ratio is estimated from Si KLL (1620 eV) and W MNN (1736 eV) peak intensities. This ratio is between 1.5 and 1.8 for deposited lines with both types of laser. Depth profiling measurements indicate a silicon depletion of a few tens of nanometers at the surface of the deposit. This Si depletion was also noticed in the preliminary results of the deposition in a static reactor [12]. This is not a measurement effect that could be attributed to differences in sputtering efficiencies, since the sputter yield is higher for Si than for W [15]. This tungsten rich surface is directly related to the nature of the deposition process. According to Lo [16], many competing, temperature dependent, reactions occur between the gaseous species and the deposited materials, even at room temperature. In laser direct writing, only a fraction of the substrate is heated at a given time. A specific location of the substrate is then submitted to the temperature rise and fall. Room temperature reactions will continue at the surface of the deposit after the beam exposure. Moreover, the Si reduction of WF$_6$ is thermodynamically favorable at room temperature, and consumes Si to produce W [16]. However, this reaction is limited to a depth of a few tens of nanometers by the diffusion of the Si atoms through the W layer [17]. This may explain the Si depletion at the surface of the deposits.

DISCUSSION

In pyrolitic laser direct writing, the laser beam locally heats the substrate surface and induces a localized chemical vapor deposition process. The temperature rise is determined by the thermal and optical properties of the substrate and the deposited film as well as by the laser power density. Since W and WSi$_2$ strongly absorb the diode laser radiation [18,19], this temperature rise is difficult to achieve only at the start of the deposition process. When deposition starts, the absorption occurs in the deposit and the temperature rapidly increases, leading to a higher growth rate. The critical step for deposition with the diode laser then is the formation of the first layers of WSi$_x$. XPS measurements show that exposure to the gas mixture partially achieve this step by inducing partial decomposition of the WF$_6$ which creates a layer ready to be transformed.

Comparing figures 1 and 2, we notice that lines deposited with the diode laser are thicker than those deposited with the Ar⁺ laser even thought, growth rates for the Ar⁺ laser are an order of magnitude higher. This is due to the high ellipticity of the diode laser spot which implies a growth time much longer (930 ms) than the one for the 2 µm circular spot of the Ar⁺ laser (20 ms). Lines deposited with the diode laser are also wider than those deposited with the Ar⁺ laser. This effect is related to the spot dimensions and the minimum width can be controlled by modifying the spot size at the sample. Lines 2.5 µm wide were deposited in the same gas conditions using the diode laser by modifying the spot dimensions [14].

Figure 2 shows that growth rate does not strongly depend on the Ar flow for lines deposited using the Ar⁺ laser at low power. Lines deposited in these conditions have a gaussian-like profile [13]. This corresponds to a regime were the growth is mostly controlled by surface reactions. However, at higher laser power, deposited thickness reaches a maximum then saturates. This maximum thickness depends on the Ar flow and decreases with increasing Ar flow. Lines deposited in these conditions have flat toped profile [13]. This indicates that the deposition in the high power regime is controlled by mass transport to the reaction zone.

For the diode laser, line thickness decreases with increasing Ar flow even for low laser power. This difference in the growth behavior for the two types of laser is due to the high difference in light absorption between the TiN substrate and the WSi$_x$ deposit for the diode laser. As previously mentioned, the deposit greatly modify the light absorption and then the deposition conditions during the growth. This effect has been observed in deposits made at different writing speeds using the diode laser. Line thickness increases, when writing speed decreases, with a ratio higher than the ratio of speed reduction [14].

CONCLUSION

The laser direct writing of WSi$_x$ on TiN from WF$_6$ and SiH$_4$ was accomplished with two different types of laser. First, with an Ar⁺ laser which gives high deposition rates, deposits 1.5 to 11 µm wide and 20 to 180 nm thick were obtained at a 100 µm/s writing speed. In the second case, we developed a compact system using a diode laser. Lines deposited in this system were 4 to 12 µm wide and 150 to 800 nm thick. W/Si ratio in deposited lines is between 1.5 and 1.8. XPS measurements show the nature of the adsorbed layer and its importance for the initiation of the deposition process at low temperature with the diode laser. This type of direct writing system based on diode lasers may play an important role in future developments of laser processing.

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PART III

Metallization