light intensity/pulse decreases dramatically below 10 Hz, see Fig. 3. This proves that the W cluster formation takes placeduring the previous laser shots and that the excitation occurs in the subsequent pulse.
For further investigation of W cluster formation we examined the influence of H_2 and Ar flows as well as laser fluence on the light intensity. By replacing Ar with H_2 and keeping the total pressure and WF_6 concentration constant, the influence of H_2 concentration on excited light intensity was measured (see Fig. 4). With no H_2 in the mixture no light was observed. After an initial steep increase in light intensity a maximum is passed and a slow intensity decrease is observed when increasing the H_2 concentration. The first part of the curve can be explained by a simple mechanism, hydrogen is needed to form W and clusters. The second part can be explained by quenching. A hydrogen quenching effect was already reported for the atomic lines of W in similar gas mixtures [4].
Using only a WF_6/H_2 gas mixture no luminescent light was obtained. As we mentioned above, excitation of W clusters in an Ar ambient yielded broad band light emission (see Fig. 2). However, without an Ar ambient the clusters did not give the luminescent light. This suggests, that Ar has an effect on the light emission process. The measured luminescent light intensity versus Ar partial pressure in an open CVD can be seen in Fig. 5. The linear part of the curve supports the idea of a collisional effect of Ar in the light emission process, but the threshold value around 2.9 mbar is not understood yet. This indicates that Ar might also have a role in the formation of the W clusters. The laser fluence also affected the light emission, see Fig. 6. A threshold value of ~60 mJ/cm^2 is required to produce light. Above the threshold, the light intensity has a nonlinear dependence of the laser energy density. Above 90 mJ/cm^2 the function seems to be linear.

Conclusions

The broad band luminescent light obtained from $WF_6/H_2/Ar$ gas mixture irradiated by ArF excimer laser at room temperature has been investigated. The light emitting medium is shown to be W clusters with a diameter of 10 to 20 nm. H_2 is needed to form the clusters. However, a high H_2 partial pressure quenches the luminescent light. The Ar seems to have a collisional role in the light emitting process and we can not exclude that the Ar might has an effect on the formation of the W particles. A threshold laser energy density is required to generate the luminescent light.

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DIODE LASER INDUCED CHEMICAL VAPOR DEPOSITION OF WSi_x FROM WF_6 AND SiH_4

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ABSTRACT

We have developed a compact and inexpensive laser direct writing system, based on the 796 nm radiation of a 1 W diode laser array for the deposition of tungsten silicides. The laser power incident on TiN substrates varies between 50 and 550 mW. Lines are deposited from a gas mixture of WF_6 and SiH_4, whose total pressure is kept below 15 Torr to avoid uncontrolled reactions. Experiments are performed in a static reactor with WF_6/SiH_4 ratios varying from 0.2 to 10. Lines written at speeds ranging from 2 to 100 µm/s have typical thicknesses and widths varying from 30 to 1000 nm and from 4 to 15 µm respectively. Auger Electron Spectroscopy (AES) shows that no fluorine is incorporated in the WSi_x film, within the limit of detection. Moreover, no oxygen, carbon or nitrogen are detected in the bulk, although some surface contamination is present. From AES measurements, the W/Si ratio is estimated to be between 1.1 and 1.4 for a reactive gas mixture of $WF_6 : SiH_4$ (1 : 3).

INTRODUCTION

Laser induced deposition of refractory metals and silicides is particularly interesting for applications in microsurgery and custom design [1-4] of circuits. Tungsten has been deposited from WF_6 using excimer [5-7], CO_2 [8,9] and ion (Ar^+, Kr^+) [1-4,10-16] lasers. In general, these laser processing systems are large and expensive. Problems related to maintenance and reliability have limited the introduction of such systems in a manufacturing environment. In contrast, semiconductor lasers are easy to operate, require no maintenance and are competitively priced. As the output characteristics, power and wavelength, of diode lasers have improved in the last few years, they are able to play an important role in industrial application of laser processing. The potential use of diode lasers for material processing and device fabrication was first reported by Arjavalingam et al. [17]. They used a 200 mW GaAlAs diode laser array, emitting at 820 nm, to deposit gold from organometallic precursors.

We report here the development of a compact and inexpensive laser direct writing system, based on the 796 nm radiation of a 1 W diode laser array, for the deposition of tungsten and tungsten silicides, from a mixture of WF_6, SiH_4 and H_2.

Since many of the materials used in microelectronics do not strongly absorb this wavelength [18], the substrate has to be carefully chosen to obtain a temperature rise sufficient to induce the WF_6 reduction reaction. We have chosen, titanium nitride (TiN) for its optical and thermal properties. Moreover, TiN is an excellent barrier layer [19] and is also used as an adhesion layer for W metallization on SiO_2 [20, 21].

Even on such an absorbing substrate, the available diode laser power is not sufficient to induce hydrogen reduction of WF_6 since that reaction requires high temperature [13]. Since it has been shown that SiH_4 can be used to obtain a low temperature reduction of WF_6 [14], such a process seems appropriate for deposition with a diode laser. However, the initiation temperature of that reaction depends strongly upon the gas mixture. We present here the diode laser induced deposition of WSi_x on TiN from a mixture of WF_6 and SiH_4.

DIRECT WRITING SYSTEM

The direct writing system is based on a cw GaAlAs diode laser array, emitting at $\lambda = 796$ nm, with a maximum power of 1 W. The beam divergence is 10° ∥ and 40° ⊥ in the two directions transverse to the propagation. The laser beam is collimated with a 0.5 NA objective and the ellipticity is reduced with a 4:1 anamorphic prism pair. The collimated beam is directed into a microscope and focused with a 25X (0.31 NA), long working distance, objective. The efficiency of the optical system is 55%, yielding up to 550 mW at the substrate.

The substrates, 100 nm of reactively sputtered TiN on 800 nm SiO_2 on a silicon wafer, are degreased 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 mechanically pumped to a base pressure of 10^{-2} to 10^{-3} Torr. Line formation is achieved by moving the reaction chamber using computer controlled XY stages having a spatial resolution of 0.1 µm. Lines are written at speeds ranging from 2 to 100 µm/s in the direction parallel to the long axis of the spot using different mixtures of WF_6, SiH_4 and H_2. This substrate is at room temperature during the experiment.

DIRECT WRITING OF WSi_x

Since W strongly absorbs the diode laser radiation [18], the temperature rise is critical only at the initiation of the reaction and the reaction is not self-limited. Because the laser power is not sufficient to induce the hydrogen reduction of WF_6, we concentrated on silane reduction, which occurs at a much lower temperature [14]. The total pressure of WF_6 and SiH_4 is kept below 15 Torr to avoid uncontrolled reactions and explosive conditions. All experiments are performed in a static reactor with WF_6/SiH_4 ratios varying from 0.2 to 10. In most cases, the writing speed is 5 or 10 µm/s.

Figure 1 shows a scanning electron micrograph of a typical WSi_x line on TiN, written at 5 µm/s, using a laser power of 115 mW at the substrate and a gas mixture of 1 Torr WF_6 and 3 Torr SiH_4. The 4 µm width line which is deposited is uniform, and the line surface is smoother than that obtained with Ar^+ laser induced deposition in a WF_6/H_2 atmosphere [16].

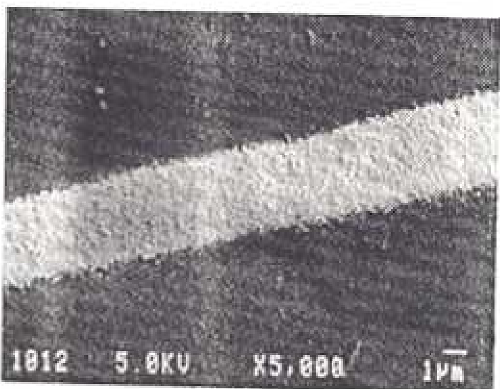

Figure 1. Scanning electron micrograph of a diode-laser-deposited WSi_x line on TiN. $P(WF_6) = 1.0$ Torr, $P(SiH_4) = 3.0$ Torr, laser power = 115 mW, writing speed = 5 µm/s.

Figure 2 shows the line thickness and width as a function of laser power for lines produced in the same conditions that we used for the line showed in figure 1. Thickness is measured with a stylus profilometer, and width is evaluated from micrographs. For a writing speed of 5 µm/s, a threshold for deposition at approximately 100 mW is observed. The line width and thickness increase with laser power. Lines produced at a power higher than 400 mW are irregular, and do not adhere well to the TiN substrate. This is due to high temperature rise of thick deposits, due to high absorption by W. These temperature rises induce thermal stress in the TiN film, causing cracking of the thin layer.

We observed, as did Black et al. [14], that increasing the SiH_4 content of the gas mixture greatly increases the reactivity and the deposition rate. Moreover, uncontrolled reactions, sometimes producing non uniform deposits up to 100 µm thick, occur for mixtures with $WF_6/SiH_4 < 0.3$. However, for $WF_6/SiH_4 > 5$ in a static reactor, deposition does not occur. We verified, with an Ar^+ laser, that the laser power required to activate these mixtures is even higher than that necessary for hydrogen reduction of WF_6. Reproducible and well controlled growth is obtained with a mixture of 1 Torr WF_6 and

3 Torr SiH_4. We are now investigating the possibility of using an Ar buffer gas, and a mixture of silane and hydrogen as the reducing gas.

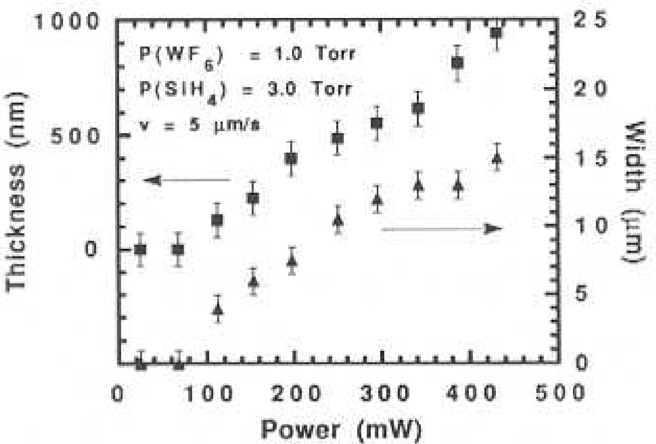

Figure 2. Thickness and width of laser deposited lines as a function of diode laser power at the substrate. $P(SiH_4)$ = 3.0 Torr, $P(WF_6)$ = 1.0 Torr, writing speed v = 5 μm/s.

Figure 3 shows Auger electron spectra for a WSi_x line written at 5 μm/s with a laser power of 150 mW. The SiH_4 and WF_6 pressures are 3.0 Torr and 1.0 Torr respectively. The spectra are shown for various Ar^+ sputtering times (sputtering rate of approximately 6 nm/min). Our analysis indicates that no fluorine is incorporated in the WSi_x film within the limit of detection. Aside from some surface contamination, attributed to atmosphere exposure, no carbon, nitrogen or oxygen are detected in the bulk of the deposited metal. After a few tens of nanometers in depth, the W/Si ratio is uniform in the bulk and estimated to be between 1.1 and 1.4. The silicon depletion at the surface cannot be attributed to the differences in sputtering efficiency, since the sputter yield is higher for silicon than for tungsten [22]. According to Lo [23], many temperature dependent, competing, reactions occur between WF_6, SiH_4 and the deposited W and Si, even at room temperature. In laser chemical vapor deposition, only a fraction of the substrate is heated at a given time. Room temperature reactions will continue at the surface of the deposit after the beam exposure. This may explain the silicon depletion at the surface. Work is underway to clarify this point.

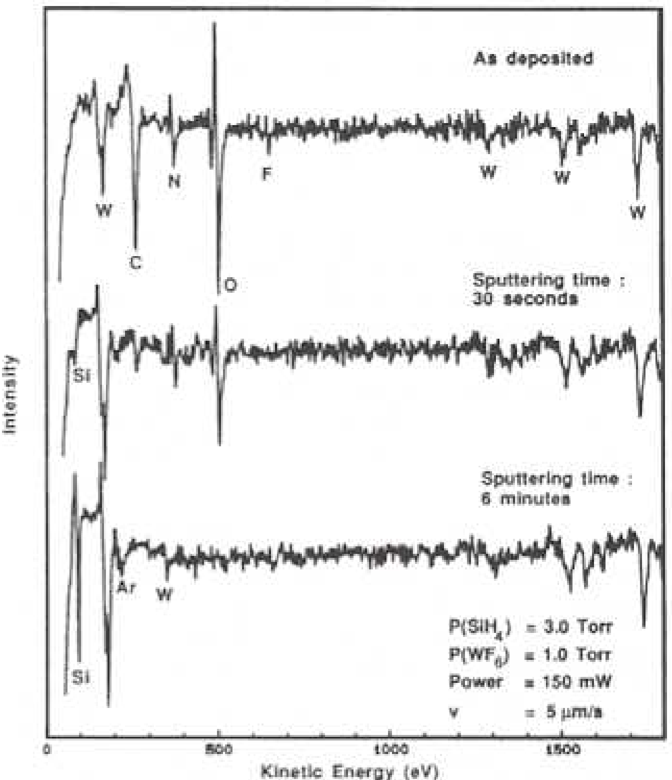

Figure 3. Auger electron spectra of laser deposited WSi_x line for various sputtering times.

V. CONCLUSION

We have demonstrated the use of a diode laser array for laser direct writing of WSi_x on TiN from WF_6 and SiH_4. The low absorption by many electronic materials in the near-infrared region has limited the direct writing to specific absorbing substrates. The development of diode lasers with more power at shorter wavelength will extend the applications of diode laser based direct writing systems to various electronic materials.

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THERMAL AND PHOTOINDUCED DECOMPOSITION PATHWAYS OF ARSINE ON GaAs(100)

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ABSTRACT

We have studied the thermal and photoinduced dissociation pathway of AsH_3 on the Ga-rich GaAs(100) surface. Arsine adsorbs molecularly at 115 K and dissociates upon either heating to above 140 K or upon irradiation with 3.5 - 6.4 eV photons. The decomposition of arsine is accompanied by the formation of surface Ga-H species, which are thermally and photochemically more stable than surface AsH_x. A comparison of the wavelength dependence for adsorbed and gas phase arsine reveals that the excitation mechanism of the AsH_3 surface photochemistry is substrate mediated, which probably involves a charge transfer between surface states and the adsorbate.

I. INTRODUCTION

The last few years have seen an increasing effort to use laser-assisted organometallic chemical vapor deposition (OMCVD) and atomic-layer-epitaxy (ALE) to enhance growth rate, to lower the growth temperature, to realize selective growth, and to control dimensions with atomic accuracy [1,2,3]. Obviously a mechanistic understanding of the surface chemistry of these processes is one key for the future development of these laser assisted technologies. However even the thermal chemistry of arsine, which is the most widely used As-precursor molecule for GaAs growth, is far from being understood [4,5]. We have therefore studied one of the fundamental reactions in ALE and laser-assisted GaAs growth: the thermal and photoinduced decomposition of AsH_3 on GaAs(100). While the details will be published elsewhere [6,7], we give here a brief report of our results.

II. EXPERIMENTAL

The experiments were performed in a UHV chamber, equipped with a high resolution electron energy loss spectrometer (HREELS), a quadrupole mass spectrometer for thermal desorption spectroscopy (TDS), a hemispherical energy analyzer and an X-ray source for X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED) optics, an ion gun for sputter-cleaning, and a pin-hole collimated molecular doser [8]. For the photochemical studies, pulsed UV light of an excimer laser with photon energies of 3.5 eV (XeF), 5 eV (KrF) and 6.4 eV(ArF) was used. The laser pulse energy was kept below 1 mJ/cm^2 to prevent desorption due to thermal heating. The samples were cut from GaAs(100) wafers (10^{15}-$10^{18}/cm^3$ Si-doped) and mounted on the edges by two Ta clips spot-welded to the sample holder. The sample could be cooled by liquid nitrogen to ~ 115 K and resistively heated to 900 K via a 4000 Å thick Ta film sputtered onto the backside. Cleaning was achieved by Ar ion sputtering, annealing (773 K), and flashing (900 K) cycles. Surface cleanliness was verified by XPS and LEED. The latter showed a (4x6)