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Effects of process temperature in the high speed, mask-less, precision laser deposition of micro-tungsten tracks on silicon, copper and stainless-steel

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Abstract

Pyrolytic laser-induced chemical vapour deposition is a technique that achieves rapid (volumetric deposition rate up to 3900 $\mu m^3 s^{-1}$), mask-less deposition of metal and ceramics on numerous substrates such as steel, fused silica, silicon and polymers. The technique can be used for a range of applications one example being writing conductive micro-tracks for the construction of nano- and micro-devices. In pyrolytic laser-induced chemical vapour depositions, the process temperature affects the geometry, purity, microstructure and resistivity of the deposited track and the integrity of the underlying substrate. In this paper, tungsten micro-tracks are deposited from tungsten hexacarbonyl precursors using a 405 nm diode laser on substrates such as silicon, copper and stainless-steel. The average substrate temperature during the process was measured using an infrared thermometer; the peak temperature and temperature distribution around the laser spot were estimated using a numerical heat transfer model. This paper reports the effects of the temperature on the width, height, elemental composition, microstructure and resistivity of the laser-deposited tungsten micro-tracks and the integrity of the underlying substrates.

Laser-induced chemical vapour deposition, tungsten micro-tracks, temperature effects, additive manufacturing.

1. Introduction

Laser-induced chemical vapour deposition (LCVD) generates solid deposits on substrates by initiating chemical reactions from precursor vapours at locations defined by a laser [1]. The chemical reactions in LCVD can be either photolytic (direct UV photochemical decomposition) or pyrolytic (thermal decomposition). Due to higher reaction temperatures, pyrolytic LCVD achieves higher deposition rates and lower impurities. In pyrolytic LCVD, a number of investigations have studied the effects of deposition temperature resulting from to variation of laser power and scan speed [1][2]. In this paper, the deposition temperature is altered by changing the chamber stage.

2. Experiment set-up and methods

Continuous wave output from a 405 nm wavelength laser diode (Pioneer BDR-209 Blu-ray DVD writer) was collimated and focused through a sapphire window into a vacuum deposition chamber to achieve a focused spot with diameter 6.6 µm and 350 mW power (Figure 1). A Micro-Epsilon CTLM-3 infrared thermometer was placed at an angle of 45 ° and focused on the substrate, 1 mm away from the laser spot.

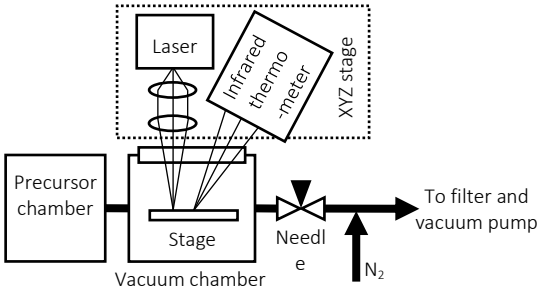

Figure 1. Schematic of laser and vacuum chamber.

Silicon wafers with 285 nm silicon dioxide coating, SS304 and copper substrates ≈8 mm square were ultra-sonically cleaned in reagent grade isopropanol for 8 mins and blown dry. During experiments, the chamber was pump to 1 Pa (measured with Edwards APG100-XLC Pirani gauge) then backfilled with 5×10^4 Pa nitrogen while the deposition chamber and stage was heated to between 80 °C -110 °C. Subsequently, the precursor chamber was heated to 80 °C. After 20 mins, the vacuum chamber was pumped to 100 Pa and the needle valve closed. Once the pressure rose to 150 Pa due to sublimation of the precursor, the laser was scanned at focus on the surface of the substrate with a power of 350 mW and scan speed 10 µm s^{-1}.

The average cross-section profiles of the deposits were measured using a Veeco Wyko NT3300 white light interferometer. The microstructure of the deposit was observed using a Zeiss Gemini 1540 XB scanning electron microscopy (SEM) equipped with a focused ion beam (FIB) for profile sectioning. The elemental composition of the deposit was analysed using an Oxford Instruments X-MaxN 80 energy dispersive X-ray spectroscope (EDX), using a beam energy of 20 kV. The track resistance was measured using a Keithley 2000 Multimeter in four probe mode with sputtered gold pads.

The laser heating was simulated in COMSOL Multiphysics 5.0 using a moving Gaussian surface heat source defined as

$$Q = P\,(1-R)\,\frac{2}{\pi\omega^2}\exp\left(-2\frac{(x-v_x t)^2+y^2}{\omega^2}\right)$$

Here P is the laser power, R is the effective substrate reflectance, ω is the e^{-2} beam radius and v_x is scanning speed. The simulation domain was limited to 10 mm × 10 mm × 0.3 mm and is divided into tetrahedral mesh elements. The bottom surface temperature of the substrate was fixed at the temperature measured experimentally.

3. Effects of temperature on height profiles

The cross-section of the deposited tungsten track on silicon exhibits triangular height profiles as seen in Figure 2 (left). The profile height and width increase with stage temperature.

When the maximum track height is plotted against the inverse of the peak temperatures Figure 2 (right), it shows a linear fit indicating that the growth is limited by the substrate temperature rather than transport of precursor to the substrate [3]. The peak temperatures of 500 °C - 600 °C were within the reported large area CVD deposition temperature of tungsten using the same precursor [4].

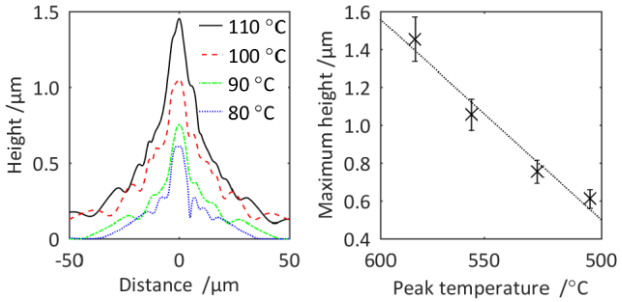

Figure 2. (Left) Cross-section height profile of deposition on silicon at various stage temperatures. The estimated height measurement uncertainty is ± 8 %. (Right) Plot of maximum cross-section height against inverse of peak temperature. Linear fit indicates temperature limited growth [4].

4. Microstructure and elemental composition

Figure 3 shows SEM images of the tungsten track deposited at stage temperature of 80 °C and 110 °C. The deposits are granular, with larger granules at the centre of the track and smaller denser granules in the outer region. When the stage temperature is increased from 80 °C to 110 °C, the size of the grains at the centre of the track increased from ≈200 nm to 500 nm leading to a rougher surface. The elemental composition at the centre of the track were ≈84 % tungsten, ≈8 % carbon and ≈8 % oxygen with no significant variation with the stage temperature. The percentage of impurities increased in the outer region. At FWHM, the tungsten percentage for the deposit with stage temperature of 80 °C is 52 %. When the stage temperature is increased to 110 °C the tungsten purity at FWHM is lower at 31 %.

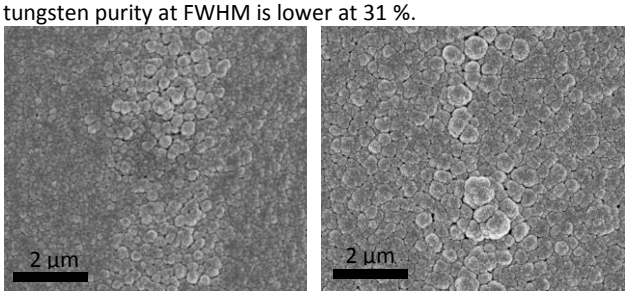

Figure 3. SEM image of tungsten deposited with stage temperature at 80 °C (left) and 110 °C (right) showing granular microstructures.

Figure 4 shows the FIB milled cross-section of the tungsten track. At 110 °C, the porosity at the top and bottom of the deposited track increased. There is no noticeable damage to the underlying silicon substrate at both stage temperatures.

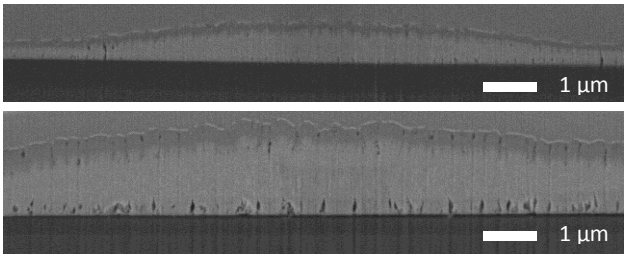

Figure 4. FIB milled cross-section of tungsten deposited with stage temperature at 80 °C (top) and 110 °C (bottom). Visually, there is higher porosity in the track deposited at a stage temperature of 110 °C.

5. Resistivity

Table 1 shows the resistivity of the tracks which increases with stage temperature. This increase is attributed to the higher porosity and lower overall purity at higher stage temperatures (section 4).

Table 1. Resistivity of deposited tungsten track on silicon increases with stage temperature.

Stage temperature /°C	Estimated peak temperature during deposition /°C	Resistivity /µΩ cm	Multiple of bulk tungsten resistivity
80	505	892	159
90	527	1296	232
100	556	2731	488
110	583	3524	629

6. Stainless steel and copper results

The estimated peak deposition temperature on stainless steel, silicon and copper are 1041 °C, 583 °C and 183 °C respectively. The peak temperature in stainless steel is highest due to its lowest thermal conductivity. The cross-section height on stainless steel, silicon and copper deposited at a stage temperature of 110 °C (Figure 5) agrees with section 3 where the width and height of the track increase with peak temperature. The microstructure of the deposits on stainless steel and copper are also granular. The high peak deposition temperature on stainless steel leads to large grains around 1 µm in size and thus a very rough track.

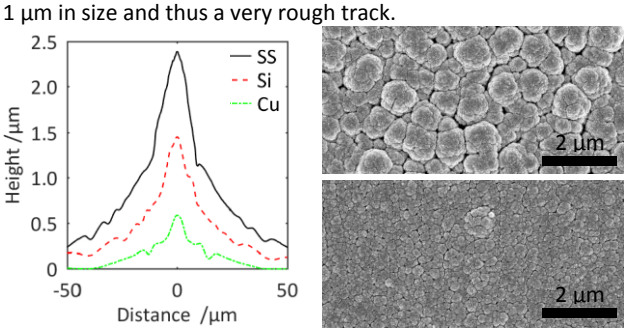

Figure 5. Cross-section height of deposited track on various materials with deposition stage temperature of 110 °C (left). The estimated height measurement uncertainty is ± 8 %. Microstructure of deposit on stainless steel (top right) and copper (bottom right) showing granular structures similar to that seen in deposition on silicon.

7. Conclusion

Variations of 10 °C in the stage temperature during pyrolytic LCVD of tungsten from tungsten hexacarbonyl leads to significant differences in track height, width, microstructure and resistivity. For deposition on silicon, the lowest stage temperature of 80 °C produces the best track resistivity of 892 µΩ cm due to low porosity and overall track purity.

References

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