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ARTICLE

Supplement to Enhanced material purity and resolution via synchronized laser assisted electron beam induced deposition of platinum

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Thermal simulation of laser-substrate interaction

A 1-dimensional explicit finite difference method simulation of substrate heating with pulsed laser irradiation was built for estimating the temperature over time and into the substrate. The spatial resolution of the simulation grid of the substrate was varied and was a minimum of 10 nm at the near surface region. The time step of the simulation was maximized while still ensuring stability. The laser pulse was given a rise time of 10 ns, which was measured from the laser at 186 kW/cm^2 irradiance operation. The substrate was initially at thermal equilibrium at 300 K. A radiative cooling boundary condition was imposed on the substrate surface with a surrounding temperature of 300 K. The backside of the substrate was given an insulating boundary condition. In the simulations performed (laser pulse width and irradiance) no temperature rise was measured in the near backside region. Simulations were performed for various substrate materials and laser pulse widths and irradiance to estimate the time-temperature profile of the surface temperature as well as the thermal penetration depth. Due to the short time steps (typically on the order of 10^{-13}), a realistic limit was placed on the maximum laser pulse width (100 µs). Properties of the substrate materials were selected at 300 K and assumed to remain constant for the full temperature range. This assumption was used as no phase change was expected for the pulse widths and irradiances simulated. Table A1 shows the properties of the substrate materials used for the simulations.

Table A1. Material properties at 300 K and 915 nm for the simulation of laser substrate heating.

Property	Ti	SiO_2	Si
Reflectivity	0.547	0.000	0.323
Absorption (1/cm)	4.48E5	5.07E2	3.14E2
Thermal Conductivity (W/cm-K)	0.219	0.014	0.149
Specific Heat Capacity (J/g-K)	0.540	0.937	0.700
Density (g/cm^3)	4.510	2.200	2.329

Fig. A1 shows finite difference methods simulation of our laser pulse on the substrate (50 nm Ti on 100 nm SiO_2 on Si). Demonstrated in this figure is the impact that pulse power, as well as pulse width, has on the surface time-temperature profile and the thermal penetration depth. Based on these simulations short and high-powered pulses were utilized in the following LAEBID experiments, in order to minimize the time required for efficient thermal desorption of the by-product while allowing enough time for precursor coverage to refresh. Fig. A1 demonstrates that the temperature of the substrate surface cools to the ambient temperature long before the typical refresh period of 100 ms is complete, resulting in steady-state precursor coverage for the next electron beam dwell cycle.

Resistivity measurement

Four point probe measurements were performed on eight point probe devices. The eight point probe devices were fabricated using electron beam lithography followed by electron beam evaporation of a Cr adhesion layer (5 nm) and an Au layer (100 nm). Fig. A2(a) shows an SEM image of the full device with eight electrode contact pads. Of the eight probes depicted in Fig. A2(b), only the right four probes were used for measurements. Fig. A2(b) shows the current source and drain as well as the two voltages measurement probes. Fig. A2(c) shows an SEM image of an EBID line tilted 60° and rotated 30° and (d) shows an SEM image of a LAEBID line with a 50 µs pulse width and 186 kW/cm^2 irradiance tilted 60° and rotated 30°.

Standard four point probe measurements were made by forcing a source current from 0-10 µA (250 nA increments) between the outer two probes (see Fig. A2(b)) and measuring the appropriate voltage drop between the inner two probes. Subsequent to the electrical testing, each line was focused ion beam cross sectioned and imaged via high-resolution scanning electron microscopy (Fig. A2(e)) to accurately determine the cross-sectional area (A) for the resistivity (ρ) determination, where ρ=RA/L and the length (L) was defined by the inner probe separation (1.5 µm). Fig. A3 shows current-potential plots for the lines shown in Fig. A2(c) and (d).

Anneal Comparison

A post-deposition thermal treatment was performed on both EBID and LAEBID structures with a 5 keV, 400 pA electron beam with a dwell time of 50 µs and 10 µs width laser pulses at an irradiance on the sample of 186 kW/cm^2 for a total of 1000 loops. Fig. A4 shows the atomic concentration of platinum before and after a 1-hour 250 °C hot plate anneal in ambient conditions along with SEM images of each. The improvement seen in the

EBID structures is similar to results from Botman et al.[1]. These results show that annealing the LAEBID structure is not as effective as that of the EBID structure. This difference in purification is likely due to a change in the structure of the carbonaceous matrix in which the platinum is embedded. While it is opined that the LAEBID carbon is likely graphitized during the process, additional measurements need to be made to accurately understand why annealing is less effective on the LAEBID structure compared to the EBID structure.

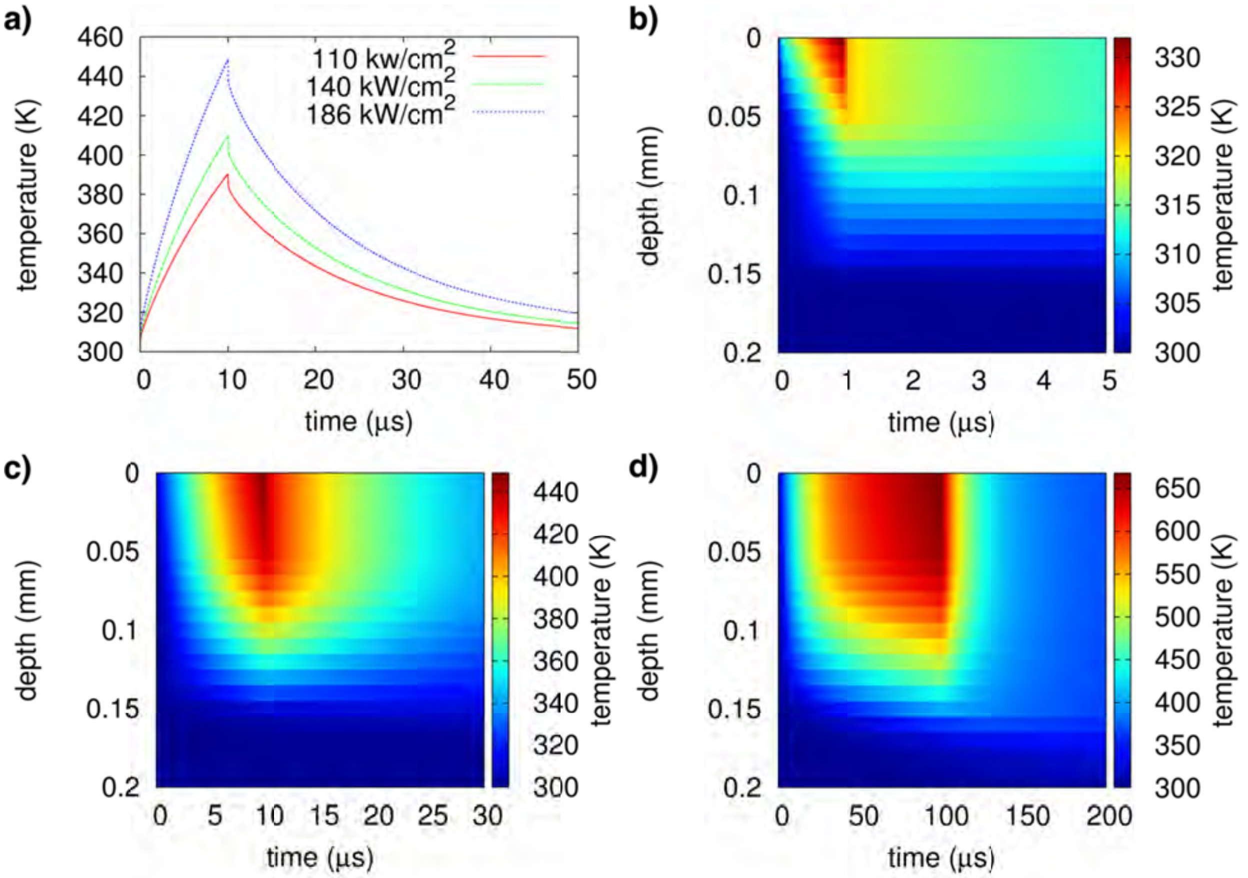

Fig. A1 Plot of FDM simulation of temperature evolution of the substrate. (a) Time evolution of the surface temperature of a 50 nm titanium film on a 100 nm thermal oxide on a silicon substrate irradiated with 10 µs pulse widths of different irradiances. (b-d) Temperature map of the thermal penetration of the substrate irradiated with three different pulse widths of the same irradiance (1 µs, 10 µs and 100 µs laser pulse widths, respectivitly).

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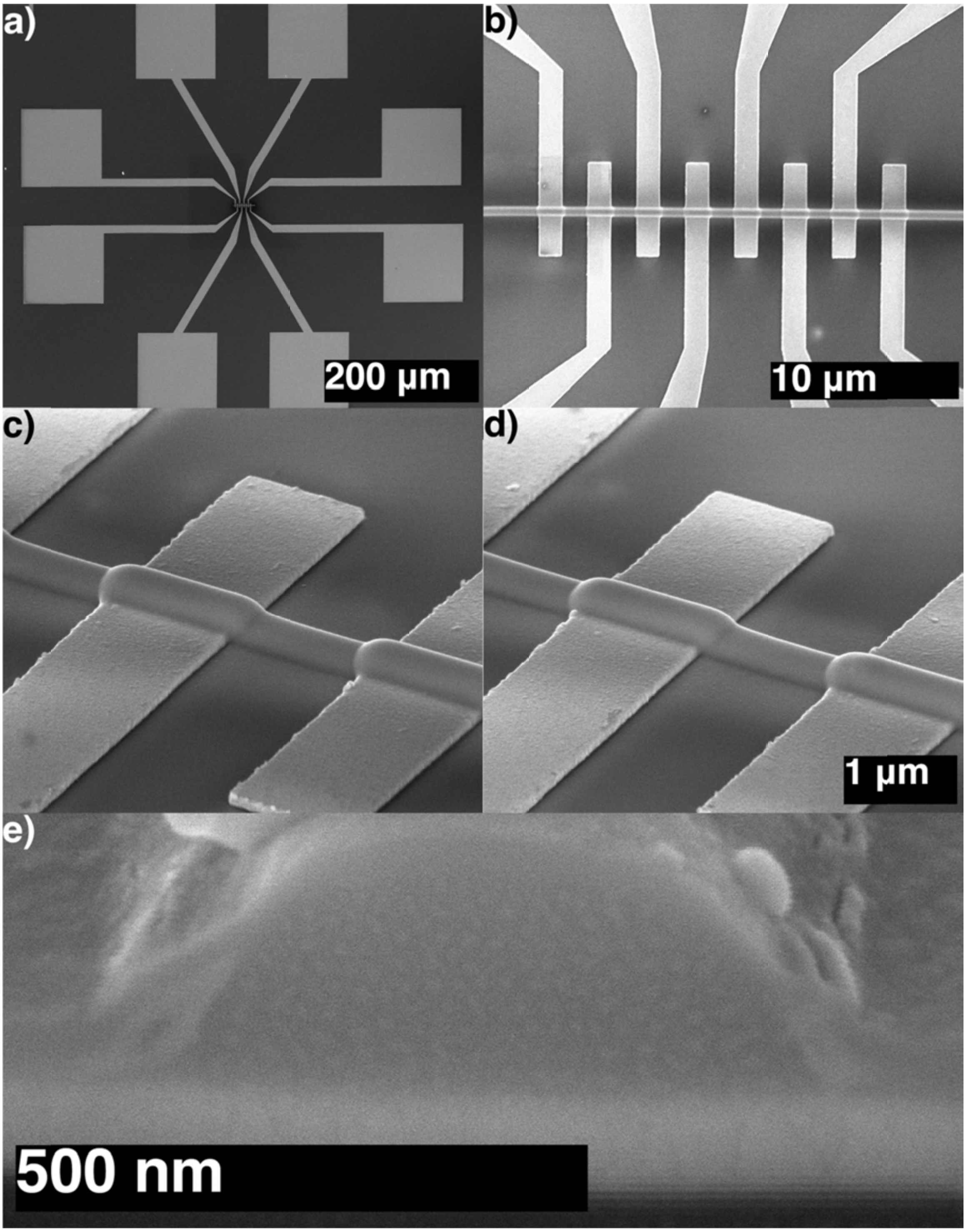

Fig. A2 SEM images of (a) the total eight point probe device used for the four point probe measurements, (b) a higher magnification image of the probe finders with an EBID line deposit, (c) and EBID line tiled 60° and rotated 30° and (d) an LAEBID line with a 50 μs pulse width and 186 kW/cm^2 irradiance tilted 60° and rotated 30°. (e) An example tilted focused ion beam cross-section of the line deposit in (d).

Electronic Supplementary Material (ESI) for Nanoscale

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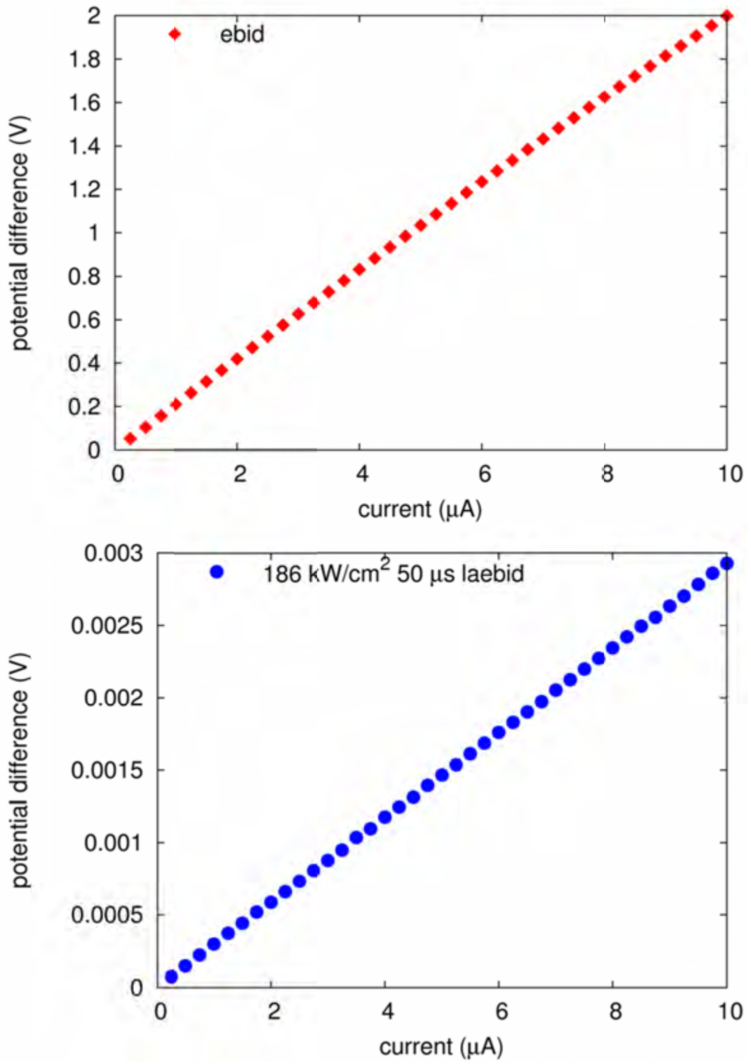

Fig. A3 I-V curve from four point probe measurements for (a) EBID and (b) 50 µs pulse width and 186 kW/cm^2 irradiance LAEBID lines.

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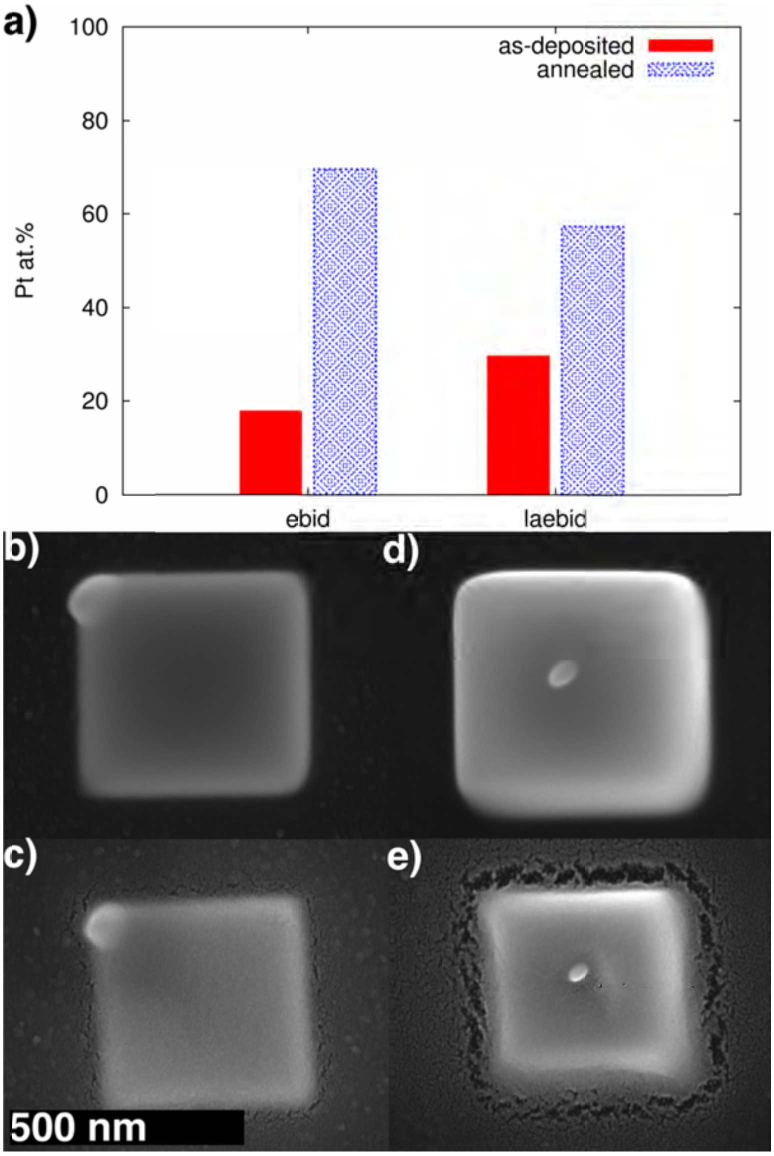

Fig. A4 (a) Atomic concentration of EBID and LAEBID platinum before and after a 1 hour 250ºC hot plate anneal. (b-c) SEM images of the LAEBID before and after annealing. (d-e) SEM images of the EBID before and after annealing. (note the observed difference in change for the EBID in purity and the structure versus the LAEBID deposit).

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