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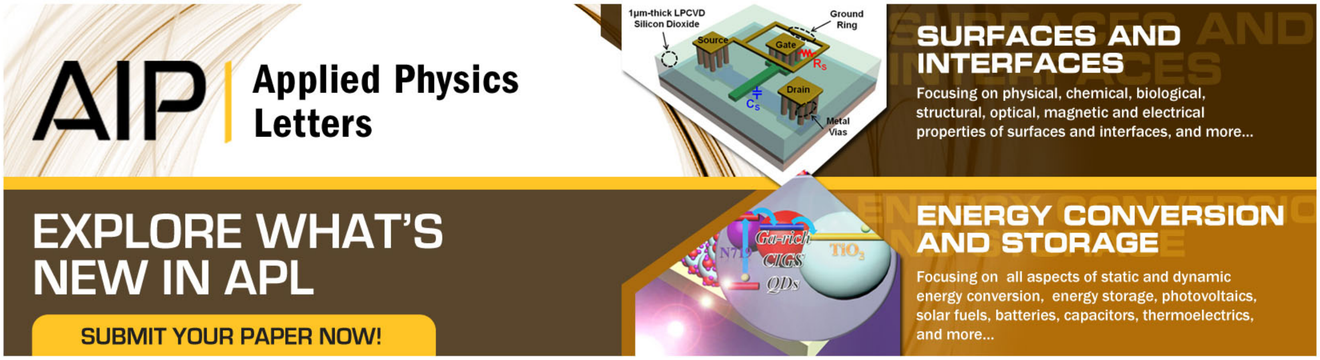

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Tip-based chemical vapor deposition with a scanning nano-heater

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In this preliminary effort, a moving nano-heater directs a chemical vapor deposition reaction (nano-CVD) demonstrating a tip-based nanofabrication (TBN) method. Localized nano-CVD of copper (Cu) and copper oxide (CuO) on a silicon (Si) and silicon oxide (SiO_2) substrate from gasses, namely sublimated copper acetylacetonate ($Cu(acac)_2$), argon (Ar), and oxygen (O_2), is demonstrated. This technique is applicable to other materials. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4799654]

Scanning thermal probes,[1] developed for atomic force microscopy (AFM),[2] can be used as nano-heaters to create localized manufacturing environments. Existing nanomanufacturing technologies have several limitations such as inability to control the manufacturing process in real time and uniformly grow a material.[3,4] AFM tips may provide a nanomanufacturing solution, as a result TBN has become a viable alternative for next generation nanofabrication.[3] There are a number of TBN platforms, ever since IBM's Millipede[5] that utilized nano-heater arrays. These platforms include dip pen nanolithography,[6] nanoembossing,[7] tip-based nano-electromachining,[8] nano-electrochemical machining, deposition and transformation,[9] and tip-based laser assisted nanomanufacturing.[10] There have been efforts to thermo-chemically pattern organic materials[11,12] and to thermally reduce graphene oxide[13] using nano-heaters. Other efforts have concentrated on 2-dimensional precision patterning on Si.[14] However, TBN has mainly concentrated on chemically, mechanically, or thermally altering substrates in 2-dimensions or depositing liquid chemical reagents.[4]

In this letter, a moving nano-heater locally heats specific areas on a substrate to induce a chemical reaction from precursor and reaction gasses for the deposition of materials. More specifically, $Cu(acac)_2$ and O_2 were used resulting in the deposition of Cu and CuO at desired locations. The tip-contact area has a diameter of sub-micron lengths, heating the substrate over a diameter that is similar to the tip. The tip is heated resistively and the nano-heaters are designed so that most of the heating occurs at the contact area.[15–17]

The nano-heater includes a metal resistor that acts as a heating element, made of 10 nm Ti and 100 nm Ir film, with nominal resistance of 8.15 Ω, deposited on a Si and SiO_2 cantilever. The fabrication of the nano-heater is described in prior publications.[15–17] The nano-heater comprises of a 20 μm tall tip with a <500 nm tip diameter and a passivation layer covering the cantilever and the tip made of a 100 nm Si_3N_4 layer. The device is annealed at 900 °C for 2 h. It is operated at 288 mW by passing current through the resistor, which corresponds to a temperature of approximately 298.8 °C at the tip. The nano-heater is calibrated using a thermocouple.[15]

A custom made scanning system, illustrated in Fig. 1(a), resides inside a glass chamber. The tip is scanned using an XYZ piezo-electric stage (Tritor 100 XYZ piezo-positioner from Piezosystem Jena) with 0.2 nm resolution and motion range of 100 μm in each direction. A motorized stage (KT-LS28-MV from Zaber) is used to align the probe tip to the desirable scanning region on the sample. An optical microscope is used to monitor the probe tip and the sample movement. Four connectors are fitted on the sidewall of the chamber, one for gas inlet, one for gas outlet, one for electrical connection feed-through, and one for pressure monitoring. The inlet is connected to tubes that connect to flow-meters that in turn connect to gas cylinders. The outlet is connected to a pump. The sample holder rests on top of the piezo-positioner and includes a flat heater (Omega) attached on one side and a substrate on the other. The thermal probes are heated with a sourcemeter (Keithley 2400).

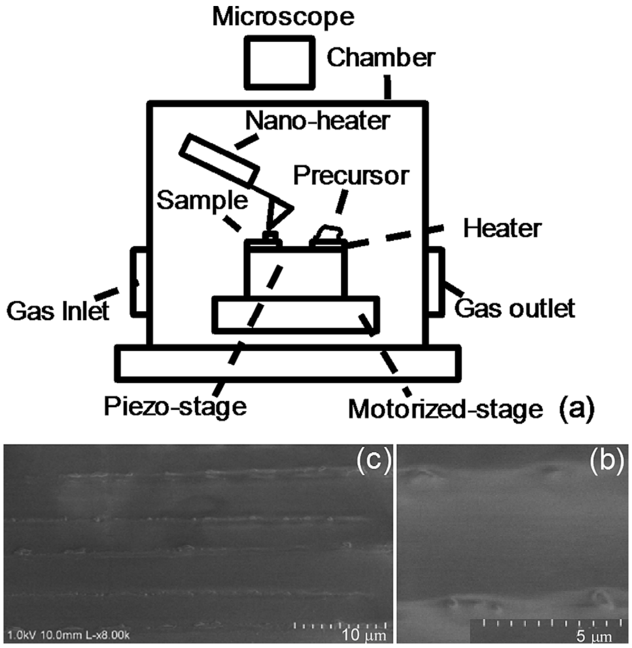

FIG. 1. Nano-CVD using a nano-heater. (a) Schematic of the set-up. (b) SEM image of the fabricated lines is in agreement with the tip's movement. The tip was stopped for 10 s every 5 μm in the X-direction and moved by 5 μm in the Y-direction. The Cu and CuO lines can be clearly seen. (c) A higher magnification SEM image showing sub-micron structures repeated every 5 μm.

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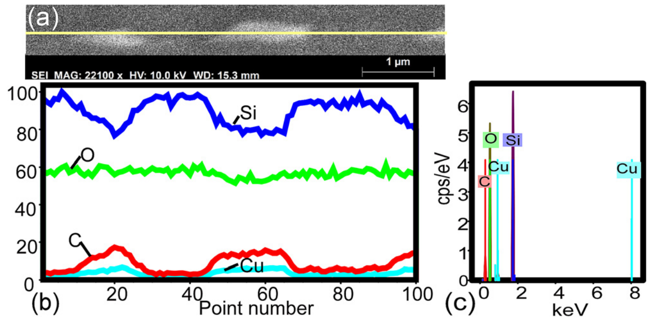

FIG. 2. Chemical analysis of nano-CVD. (a) Prior to performing the EDS line scan, an SEM image of the sample is acquired. A line marks the part to be analyzed. (b) Line scans of one dimensional normalized concentration profiles to determine the chemical elements demonstrate that C and Cu concentrate in the regions that the features are observed, while Si is mostly concentrated in the areas where Cu and C are not present. (c) The average quantitative spectrum analysis for the whole scan line indentifies and measures the individual elements' concentrations over the range of the scan line. The elements that are present include Cu, C, Si, and O_2.

Contact is determined by monitoring the tip optically through a high resolution microscope.[17]

A low-pressure metal oxide CVD process is used to grow Cu and CuO from $Cu(acac)_2$ ($C_{10}H_{14}CuO_4$). The chemical reaction and conditions such as pressure and temperature are described in Condorelli[18] and Condorelli.[19] Ar and O_2 are introduced under constant flow rates of 200 sccm for O_2 and 30 sccm for Ar, respectively. The total pressure is held between 4 Torr and 5 Torr. $Cu(acac)_2$ was obtained in powder form[20] and placed on the flat heater inside the chamber in close proximity to a Si/SiO_2 diced wafer substrate. $Cu(acac)_2$ is then heated to a sublimation temperature of 130 °C. The nano-heater is brought in contact with the substrate and heated to approximately 298.8 °C. The piezoelectric stage is programmed to move a total area of 70 μm by 70 μm. The X-axis is set to stop every 5 μm for 10 s and the Y-axis is programmed to move by 5 μm following a full 70 μm X-axis movement.

Scanning electron microscope (SEM) (Hitachi SU8000) images and energy-dispersive X-ray spectroscopy (EDS) (QUANTAX by Bruker) chemical analysis demonstrate that Cu and CuO features are consistently obtained by scanning the nano-heater over the substrate (Figs. 1 and 2). The SEM images (Figs. 1(b) and 1(c)) demonstrate that CVD growth occurred at the areas where the probe tip was programmed to stop for 10 s. There is some growth on the line of movement because the tip is kept at an elevated temperature even while in motion. Chemical analysis in Figs. 2(b) and 2(c), over the area shown in Fig. 2(a), confirms the presence of copper and carbon in selected regions where the heated tip is scanned and mostly accumulated at the spots that the tip stopped for 10 s.

In this preliminary study heated scanning tips were used to fabricate nanostructures. Several materials can also be grown on the substrate eliminating the need for multiple fabrication steps. Localization and control of heat allows the user to change conditions at the level of individual nanostructures enabling research in the thermodynamics and kinetics of growth. Applications are found in semiconductor and nanodevice manufacturing, functionalizing surfaces and electrically connecting nanotubes, and other nanostructures by growing electrically conductive lines. Future experiments will include controlling growth by intermittent heating and cooling, vertical growth, applying of an electric field between the tip and the substrate, exploration of additional chemistries, and high throughput growth using multi-probe arrays.

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