SYNOPSIS

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Electric Field Induced Phenomena: Mass Flow and Chemical Reaction- based Patterning

Numerous electric field induced phenomena have been studied, for long, at various length scales. In particular, a concentrated electric field applied across a conductor, or equivalently an electric current of very high density passing through a conductor, can manifest in form of both destructive and constructive processes, depending on the requirement of an application. For example, electromigration, which is diffusion-controlled electric field directed mass transport phenomenon, often leads to formation of voids and hillocks in metal interconnects in microelectronic devices (see **Fig. 1a**). This results in failure of the device and hence this “destructive” manifestation of the electric field is considered as a “villain”. On the other hand, recently discovered electromigration in liquid metals may pave the path for various useful applications, such as maskless conformal coating (see **Fig. 1b**), pattern formation, surface modification, etc. Besides the exploitation of the capability of electric field for transporting matter (e.g., in liquid metals) in controlled and directed fashion in various applications, harnessing the unique potential of electric field in inducing chemical reaction in controlled fashion in a confined region provides new avenues for constructive usage. In particular, the electric field induced chemical reaction has been exploited for patterning at extremely small length scale, using scanning probe microscope, such as atomic force microscope (AFM) and scanning tunneling microscope (STM) (see **Fig. 2**). It is imperative to unambiguously understand the fundamentals of the concerned phenomenon before the aforementioned electric current induced phenomenon can be exploited to bear numerous technologies and applications.

(a) (b)

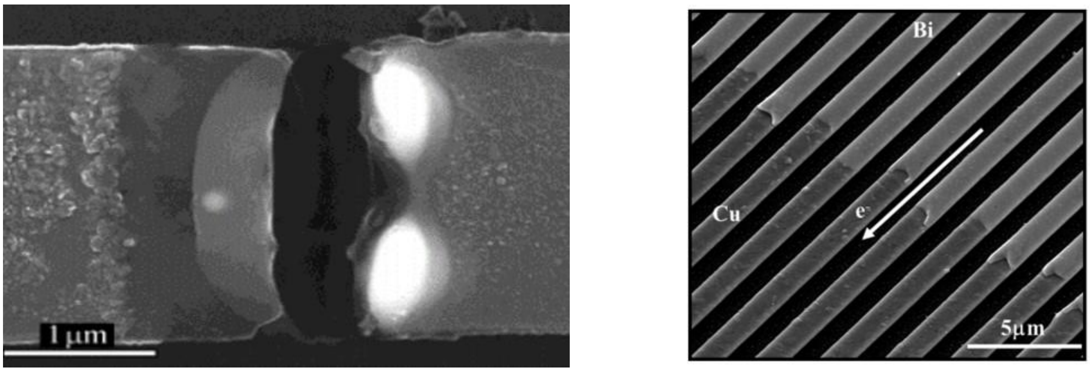


Fig. 1: Examples of (a) destructive and (b) constructive manifestations of very high electric fields. In (a), Pd thin film interconnect has broken due to electromigration, whereas in (b) liquid Bi has flown over Cu to conformally coat it.

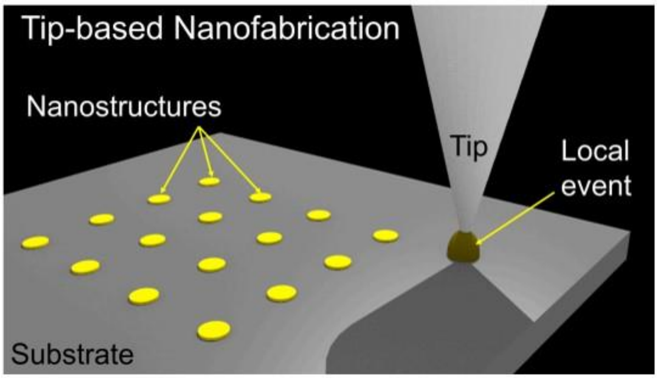


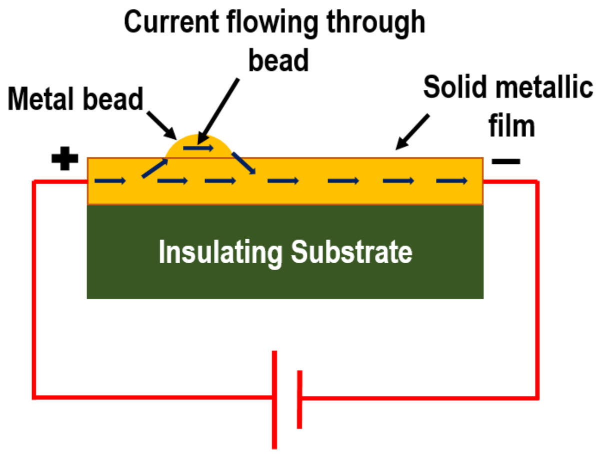
Fig. 2: A schematic illustration of electric field induced chemical oxidation process using AFM tip; this can be used for pattern generation.

Here, we have studied at two significantly different electric field induced phenomena, namely electromigration in liquid metals and electric field induced chemical reaction in solid thin metals[1]. The presentation of the study in form of this thesis is divided into three main parts, (i) Theoretical modelling of electromigration in liquid metals (or liquid electromigration), (ii) Study of the electric field induced chemical reaction in Cr film, including a detailed investigation of effects of ambient conditions on reaction kinetics, and (iii) Development of a tool for pattern drawing by the means of electric field induced chemical reaction.

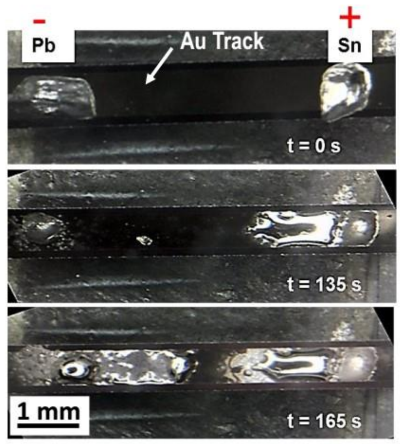
[1]The reason for studying two different phenomenon is quite interesting: As it will be explained in the thesis, we thought the two manifested phenomena (of the linear flow of liquid metal from the anode to the cathode on a conducting substrate and the radially outward flow of Cr film, deposited on Si, at the cathode) to have the common root in the electromigration in liquid metals. However, later we realized that while liquid metal flowed on a conductive substrate due to the liquid electromigration, the liquid material flowed on the non-conductive substrate due to chemical reaction occurring at the cathode.

As mentioned earlier, electromigration, irrespective of whether it is in solids or liquids, is a diffusion-controlled directional mass transport phenomenon that is driven by the applied electric field. The direction of the mass transport, in general, depends on the net force experienced by the positively charged ions due to the applied electric field and the momentum transferred from the colliding free-electrons. Hence, it is critical to understand the direction of this effective force in metal. Often it is from the cathode to the anode in a solid metal; however, it is not that straightforward in liquid metals. For example, the direction of the net mass transport in most of the liquid metals, e.g., Ga, In, Ga, etc., is in the direction of the electric field (i.e., from the anode to the cathode, which is contrary to the solid metals), whereas the direction of the flow is reversed in the liquid Pb (see **Fig. 3**).

(a)



(b)



(c)

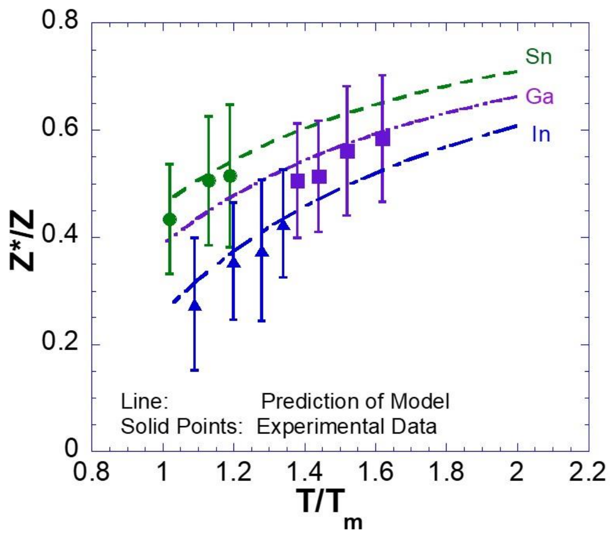
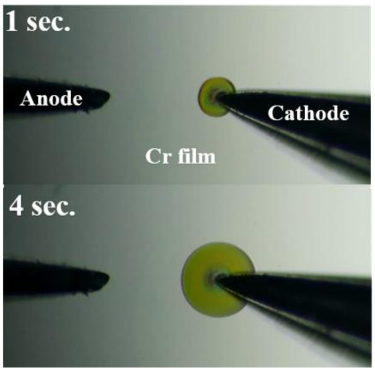


Fig. 3: (a) A schematic illustration of an experimental setup that can be used to study electromigration in liquid metals. Here, an electric current is passed through a solid thin film over which a bead of liquid metal is placed and then the ensuing flow of the liquid metal is observed. (b) A snapshot showing the dichotomy in the flow direction of liquid Pb and liquid Sn. (c) A comparison of the value of Z*, whose sign determines the direction of liquid metal flow, as predicted by the developed model and estimated experimentally.

The reason for the dichotomy of the directionality in the liquid metal flow was not completely understood and hence we performed a detailed analytical and experimental work to resolve it. Here, we developed a theoretical model based on the cell model of liquids and incorporating Lennard-Jones interaction potential. The model considers the short-range order in liquid metals and calculates the force on the ions due to the momentum transferred by electrons during electron-ion collisions. The model not only successfully predicts the flow direction of numerous liquid metals, including liquid Pb, Ga, etc., but it also gives the value of effective charge number of liquid metals as the function of the temperature. Experiments were performed on a selected liquid metals in order to validate the model (see **Fig. 3c**).

As mentioned earlier, electrical interaction between the tip and the metal (e.g., Cr) film induces a chemical reaction in the localized region around the probe tip on the film (see **Fig. 4a**). If the probe is translated over the metal film along a predefined path, then the chemical reaction induced controlled patterning of the film can be achieved (see **Fig. 4b**). In the second segment of our work, the focus has been to understand the mechanism of the phenomenon of electric field induced chemical reaction by performing a series of experiments using a custom-built experimental setup, so that we can later exploit the gained understanding for lithography. The phenomenon was studied using a W-tip with a diameter of 20 μm under stationary tip condition. Although this length scale is relatively larger than that of using AFM or STM tip, it provides significant amount of reaction product and allows easy maneuverability as well as better control of the experiments: Both of these are critical for unambiguous understanding of the nature and kinetics of the chemical reaction. The study includes confirmation of observation of a chemical reaction induced process in presence of electric field (as per Faraday's law) and the identification of the reactants (as Cr and H_2O – in form of both vapor and liquid) and the product (as CrO_3) at the cathode. The ambient conditions affect the reaction kinetics at the cathode probe tip (see **Fig. 4c**) and hence the dimensions (as well as quality) of the patterns. Therefore, the phenomenon was studied under different ambient conditions, such as vacuum, gaseous (e.g., N_2, O_2 and air) environments, variable humidity, high and low temperature, etc. It was observed that reaction did not occur in an environment unless water vapor (or water) was present. Furthermore, the reaction occurred without generation of significant amount of heat (and hence negligible rise in the temperature was associated with this process). Finally, the reaction was favored at the locations of high current densities at or near the cathode. Study on the understanding the nature of the reaction product revealed that CrO_3 is highly hygroscopic and it quickly acquires water from the air to become liquid. As the reaction product is soluble in water, the region where reaction had taken place could be easily removed by dipping the sample into water. Use of water in the reaction was further exploited to develop a new SPM based lithography process that can preclude the need of keeping the sample and the tip into contact and proffers spontaneous removal of the reaction product. Overall, the results obtained in this segment of the work paves the path for developing a new tip-based lithography technique that is better suited to meet the challenges of tip wear, debris collection, low throughput, etc., which are often associated with other SPM based lithography techniques.

(a)



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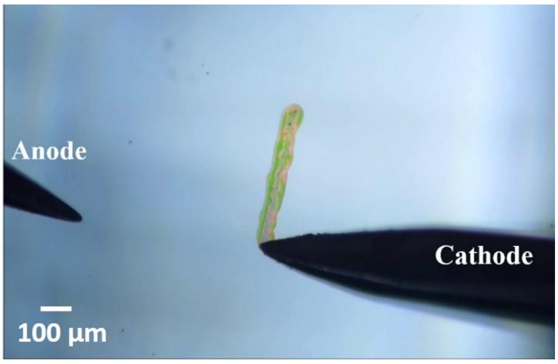

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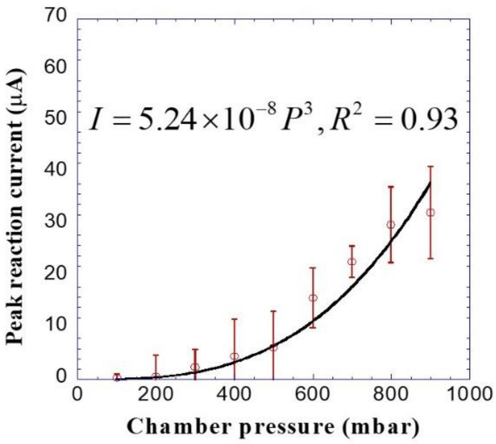

Fig. 4: Snapshots showing (a) ring pattern formation at the cathode tip touching Cr thin film (deposited on SiO_2/Si substrate) upon application of an electric field and (b) pattern drawing in Cr by traversing the cathode tip. (c) Variation of the reaction current as function of the pressure (of air) in a vacuum chamber. The equation for the best curve-fit, along with the regression parameter (R), is shown in legend in (c).

In the last segment of the work, the understanding of the electric current induced chemical reaction in Cr film was applied to develop a tool for drawing patterns at micrometer length scale. A considerable amount of effort was made to assemble a standalone lithography unit that can work in ambient as well as submerged in water conditions. Here, a micro-positioner was used to place the sample at a desired location relative to the tip, and a W tip was traversed over the sample. The tip was brought into contact with (and detached from) sample using an “electromagnet-based lever-type drive”. A software-hardware interface was developed using LabView software, which was also capable of importing drawings made in third-party software, such as CleWin. Tool parameters, such as tip velocity, tip force, etc., were observed to have significant impact on the pattern dimensions. Finally, several patterns, including closely spaced parallel lines, were generated using the developed tool in Cr films of different thicknesses and statistical information were obtained.

In summary, this work, which includes both exploration of fundamentals and application of the learned fundamentals to develop new technology for lithography, confirms the constructive potential of the electric current and invites researchers to explore this area further.