Research Report

KVPY Summer Project

Wetting behavior of microwave plasma generated low energy inert gas ion beam irradiated metallic surfaces: effect of contamination and aging.

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Acknowledgement

The research project "**Wetting behavior of microwave plasma generated low energy inert gas ion beam irradiated metallic surfaces: effect of contamination and aging**", carried out in the Laboratory of Prof. Sudeep Bhattacharjee, Department of Physics, Indian Institute of Technology – Kanpur, in itself is an acknowledgement to the inspiration, drive and technical assistance contributed to it by many individuals. The project and its report work would have never been completed without the guidance and assistance that I received from time to time during the whole research process.

I would like to extend my sincere gratitude to my supervisor **Prof. Sudeep Bhattacharjee** of the Department of Physics, Indian Institute of Technology – Kanpur, for his kind guidance, cooperation and provision of every possible required resource during the project work.

I thank **Sanghamitro Chatterjee,** Ph.D student working in the laboratory of Prof. Sudeep Bhattacharjee, for providing me unconditional support and an opportunity to enhance my skills in the field of my project. I would also like to thank all other laboratory members for their help during the experiments.

Above all, I am grateful to almighty **God** for giving me power to complete this project.

Abstract

Experiments have been performed to explore the effect of low energy (0.5 keV) Ar^+ beam irradiation on the surface wettability of metallic (Au, Al, Cu) thin films (~ 200 nm). Observations reveal a transition from hydrophilic to hydrophobic nature which was earlier explained by the modification of dispersive intermolecular interaction due to the presence of implanted Ar in the near surface atomic layers of the irradiated samples. In order to investigate the possibility of any contamination (adsorption of atmospheric carbon or possible role of oxidation) affecting the results, elemental analysis was done using Energy-dispersive X-ray spectroscopy(EDS). Time dependence of the observed changes was also looked at in order to investigate the long term sustainability for any potential applications.

Introduction

Wettability is an important surface property that is related to the surface energy of the solid substrate. It is a net result of cohesive and adhesive intermolecular forces [1]. Thus, wetting is an indirect measure of surface adhesiveness. The contact angle between a liquid and a solid surface depends on the interfacial tensions at the interface of three different phases namely, solid-vapor, solid-liquid, liquid-vapor. The Young's equation [2] relates the interfacial tensions between the three phases, namely solid, liquid and gas to the contact angle that characterizes the wettability.

$$\gamma_{lv} cos\theta = \gamma_{sv} - \gamma_{sl} \quad (1)$$

Where, γ_{lv} : liquid vapor interfacial energy
γ_{sv} : solid vapor interfacial energy
γ_{sl} : solid liquid interfacial energy
θ : equilibrium contact angle

The phenomenon of wettability is interesting both from fundamental and application viewpoint. It plays an important role in many industrial processes such as lubrication, liquid coating, self-cleaning, and microfluidic devices. Therefore, control of wettability and its long term sustenance is important for many potential applications. Diverse methods for controlling the wettability of solid have been adopted which include surface coatings, chemical modification and engineering of surface roughness. All these methods destroy the metallic properties of the substrate during the transition from hydrophilic to hydrophobic nature. When using Ar implantation for that process, the metallic properties stay the same.

Motivated by the aforementioned reasons, experiments were performed including 0.5 keV Ar^+ irradiation on Cu, Al, and Au thin films (~200 nm thick), and changes contact angle of de-ionized water on such irradiated films were observed. Elemental analysis revealed that an appreciable amount of Ar is present in the surface and sub-surface atomic layers of the irradiated samples. Hence, it is believed that the presence of these implanted atomic impurities will alter the intermolecular interaction energy near the surface and can thus modify the surface energy. Ar

implantation does not induce any Hydrogen bond or acid-base/ionic interactions due to the inert nature of Ar. This is particularly beneficial because the sample retains all of its metallic properties and undergoes a transition from hydrophilic to hydrophobic which has multiple potential applications.

Experimental Details

Sample Preparation

Silicon wafers (undoped, 500 μm thick) were used to deposit metallic thin films (~200 nm thick). Since commercially available silicon wafers are likely to have a sacrificial layer of silicon oxide, which reduces its adhesion, this layer has to be removed prior to deposition. For this purpose, the silicon wafer was treated with hydrofluoric acid and then rinsed with de-ionized water. A Thermal Vacuum Coater (Fig 1) is used to deposit a 200-250 nm thick layer of the substrate metal (Cu, Al and Au) by Physical Vapor Deposition. The substrate metals were cleaned by Piranha solution to remove any organic residues and thereafter were ultrasonicated successively by Acetone, Isopropropyl alcohol and at last by de-ionized (DI) water to rinse them before deposition. The sample is hereafter preserved in a clean vacuum desiccator in order to avoid any exposure in the ambient air.

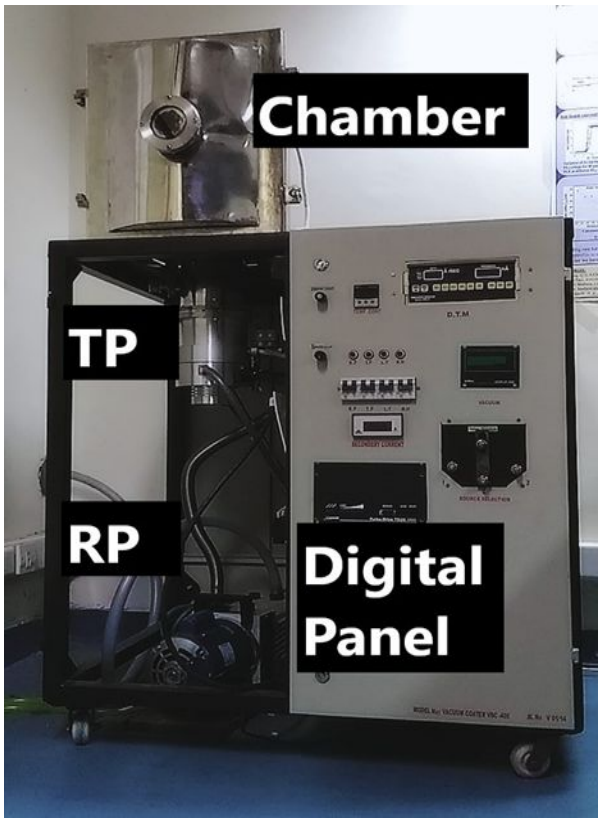


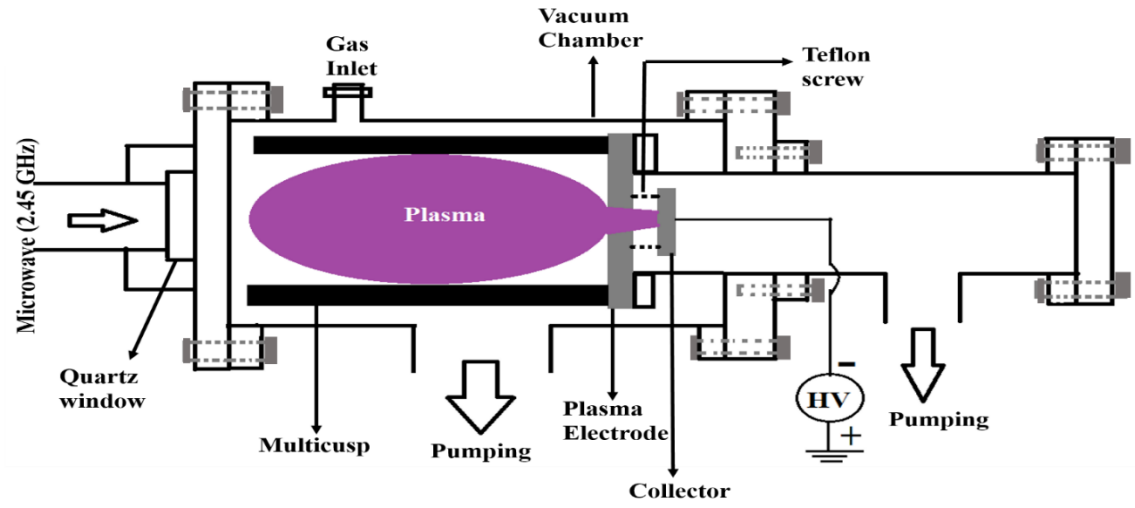
Fig 1: Thermal Vacuum Coater

Irradiation

Figure 2 (a) and (b) show the schematic and digital photograph of the experimental setup respectively. A microwave generated multicusp plasma ion source capable of delivering different

gaseous ion species, has been developed and employed in the experiment. Plasma is produced inside an eight-pole magnetic multicusp kept inside a vacuum chamber. Microwaves are launched into vacuum chamber through a quartz window. The vacuum chamber is evacuated by a turbo molecular pump to a base pressure of 10^{-7} Torr. Argon gas is introduced into the chamber through a gas inlet. The gas pressure is controlled by a mass flow controller. Differential pumping using a second turbo molecular pump in the ion beam extraction side is used to maintain a good vacuum [3,4]. During the experiment, the gas pressure in the plasma chamber is ~10^{-4} Torr.

Metallic films of 1cm × 1cm are uniformly irradiated by 0.5 keV Ar^+ beams of 2 cm diameter (normal incidence). The fluence of the ion beam was varied in a range 1.2×10^{15} - 5.2×10^{16} ions/cm^2. In our experiment, the ion fluence is adjusted by optimizing the plasma conditions (e.g. microwave power and neutral gas pressure) and irradiation time. It was observed that the metallic films were getting etched after irradiation. Furthermore, the higher the fluence, the more was the etching observed. After irradiation at the highest fluence, the remaining thickness of the initially ~ 200 nm thick Au, Cu, Al films were found to lie in the range ~ 140 – 175 nm (measured by a stylus profilometer).



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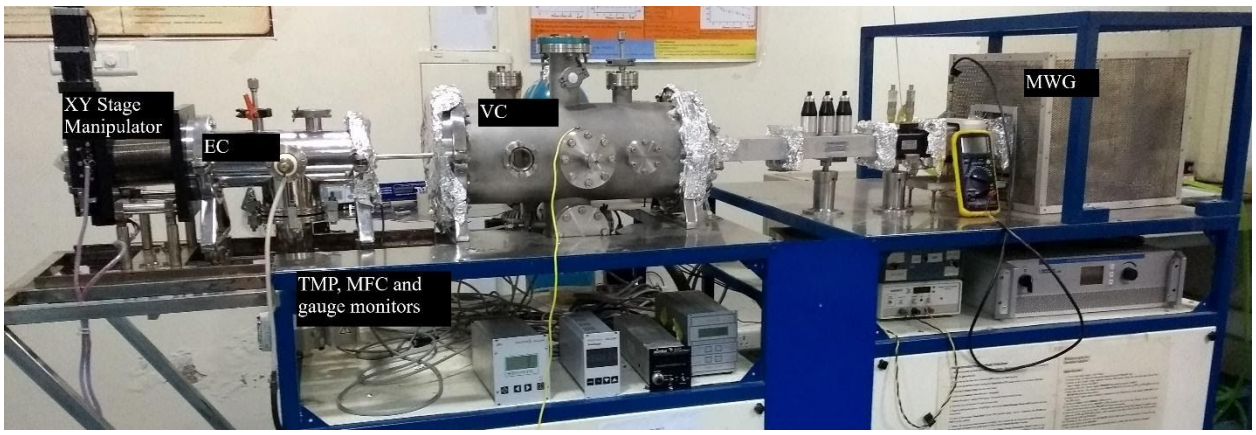

Fig 2: Experimental Setup (a) Schematic (b) Digital Photo

Contact Angle Measurement

Sessile Drop method [5] was used to measure contact angles. In Sessile Drop method, the largest contact angle possible in advancing mode of the triple phase contact line is determined by successive addition of liquid of particular volume on the initially deposited drop. This is called the advancing angle. Liquid is then successively withdrawn in the receding mode of the triple phase contact line in order to determine the smallest possible angle. This is called the receding angle.

The measurements were done in ambient conditions in a class 1000 clean room. The sample was placed on a stage. A single drop (2 µl) of de-ionized water was generated on a needle tip using a vertically clamped microsyringe. The sessile drop was formed by approaching the sample in the direction of the needle. To add subsequent drops, the stage was lifted up to the needle to place additional drops (1 µl each) on the pre-existing water drop on the sample. Thereafter, water drops (1 µl each) were removed by lifting the sample up to the needle and removing the drop by suction using the needle.

A digital camera (Nikon D7100 a digital camera with image resolution in pixels approx. 2500 × 2000 equipped with high performance "micro" lens (AF-S micro NIKKOR 60mm f/2.8 G ED) was used to capture the optical profile of de-ionized water on our irradiated sample. The high resolution digital images (fig 3) of the droplets were analyzed by drop snake analysis of the Image J® software to measure the contact angles. We define the curve of the droplet by placing knots on the surface of the droplet in the image. The contour is a circular arc for the droplet being a spherical cap in shape. The reflection of the drop onto

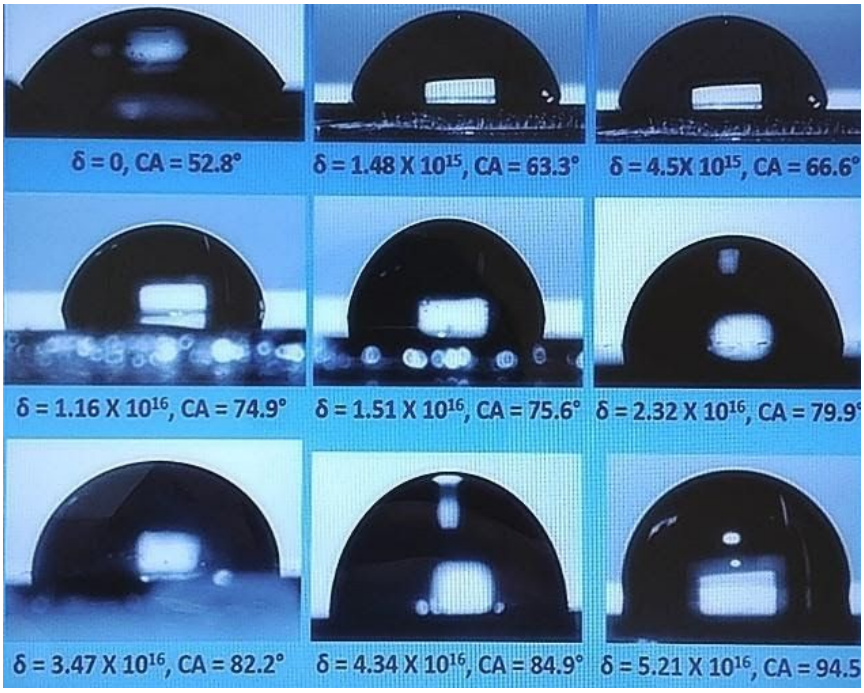

Fig 3: Digital images of Sessile drops of de-ionised water on Ar+ irradiated Au thin films

the substrate is useful, since it helps in detecting the contact points accurately. We used the average of the two values of contact angles of both side of the droplet in our measurements. Contact angles were measured on randomly chosen different locations in order to ensure uniformity.

Furthermore, these measurements were repeated five times at the interval of 5 days to investigate the time dependence of the hydrophobic nature of the metallic films. The effect of aging on the transition from hydrophilic to hydrophobic nature is of importance since if the hydrophobic nature doesn't disappear with time, this transition has many potential uses in the real world.

Elemental Analysis

Fig:4 Field Emission SEM

Elemental analysis of the sample was done at every step of the experiments, i.e., of the pristine sample, of the irradiated sample and the sample after contact angle measurements. The technique used for this analysis was Energy-dispersive X-ray spectroscopy (EDS). The Field Emission Scanning Electron Microscope (as shown in fig 4) is used for quick image analysis with high resolution and the inbuilt EDS provides compositional information. A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. In EDS, to stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of electrons is focused into the sample being studied. At rest, an atom within the sample contains ground state electrons in discrete energy

levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energies of the X-rays are characteristic of the difference in energy between the two shells and of the atomic structure of the emitting element, EDS allows the elemental composition of the specimen to be measured

We did cross sectional EDS and the elements that were specifically looked for were Carbon and Oxygen to investigate the possibility of contamination which could stem from oxidation or adsorption of atmospheric carbon in the sample during contact angle measurements.

Results and Discussion

Figure 5 shows the variation of de-ionized water contact angle (static, equilibrium) with increasing ion fluence for the three metallic film substrates of our interest. We see that the equilibrium static contact angle of water on pristine Cu, Al, Au are 66.2°, 60.5°, 52.8°, respectively indicating moderate hydrophilic behavior. With increase in fluence, the contact angle increases and there is a visible transition from hydrophilic to hydrophobic nature. From the results of fig. 5, it appears that the observed increase in the contact angle can be attributed to a significant reduction in the surface free energy of the irradiated films which is a result of the Ar atom implanted in the metallic layers.

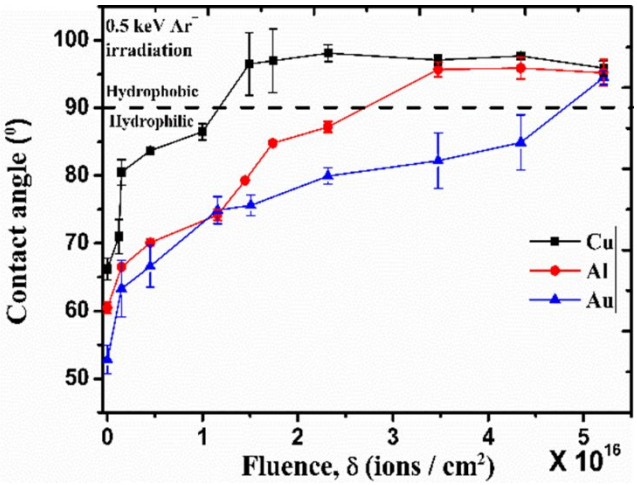

Fig 5: (Color online) Variation of static equilibrium contact angle of de-ionized water on different substrate materials (left axis) and RMS roughness of the irradiated Au films (right axis) with increase in ion fluence (δ).

The EDS studies done (fig 6) in order to look at the relative abundance of Carbon (C) on all the metallic surfaces revealed that unlike Ar, the atomic percentage of C is quite small (~8.0 - 10.9 %) and remains almost constant for all samples irradiated with different beam fluences. Hence, we believe that any modification in wettability due to the presence of C would be a constant for all fluences. Furthermore, the atomic percent of Oxygen (O) is negligibly small (~0.89 - 2.5%). It also remains almost constant with fluence. Hence, the present irradiation process does not favor appreciable chemical alterations on the metal surfaces, and the observed prominent change in wettability can be attributed primarily to Ar implantation during irradiation.

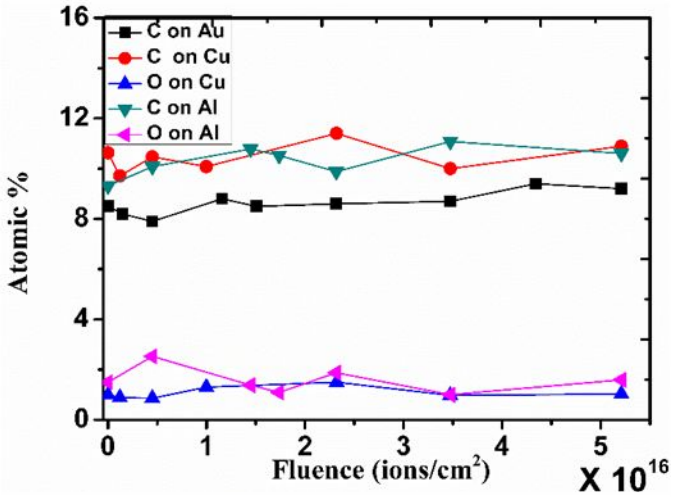

Fig. 6: (Color online) Atomic percent of C and O with respect to Au, Cu, Al, measured by EDS

Conclusion

We report that the Ar atoms implanted in the metallic layer are responsible for the change in the wettability and no appreciable amount of oxidation or adsorption of atmospheric carbon occurs during the course of the experiments.

Furthermore, it was also found that when kept in vacuum, the change in wettability of the metal surface by the irradiation does not depreciate appreciably.

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