AFM, XRD and Optical Studies of Silver Nanostructures Fabricated under Extreme Plasma Conditions

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Abstract. This paper reports the deposition of silver on silicon and glass substrates using ions generated in a 3.3 KJ dense plasma focus device. The hot and dense argon plasma formed during the focus phase ionizes the silver disc placed above the top of the anode. Glass and silicon substrates are placed at an axial position of 4.0 cm and 5.0 cm from the top of the anode and are exposed by two focus shots. The deposited materials obtained were characterized using X-ray diffraction, Atomic Force Microscopy (AFM) and UV-vis Spectroscopy. The X-ray diffraction shows the [111] and [200] reflections of silver deposited on silicon substrates whereas on glass only [111] plane is observed. The AFM of silver deposited on silicon substrates shows nanostructures which have triangular like shape. The UV spectra for silver nanostructures placed at 4.0 cm and 5.0 cm on glass substrate shows the absorption peak which originates from the surface plasmon absorption of nanosized silver particles. A red shift of ~13 nm is observed for silver deposited on glass substrate placed at the distance of 5.0 cm from the top of anode.

1. Introduction

The development of nanoscience and nanotechnology has allowed us to create new nano-sized materials having unique electronic and optical properties quite different from those of their bulk material [1]. These size-dependent properties of nanomaterials have been studied and utilized in various electronic and optical devices [2]. Simultaneously, intensive research efforts have been made to understand and control the collective properties of nanoparticles [3–5]. Metal nanoparticles have been the subject of extensive research for many years because of their anomalous electromagnetic properties originating from the resonant interaction between electromagnet waves and collective conduction electron oscillations, so-called surface plasmons [6, 7] It is well known that the plasmon resonant peak is sensitive to the size [8] and shape of the nanoparticle [9-11] and metallic species [12]. Hybrid approach for the nanofabrication can be achieved by plasma methods in laboratory. Recently, it has been established that plasma aided nanofabrication [13-14] is among the best methods of deposition. It has been established recently [13] that ions generated by high density, high temperature and extremely non-equilibrium plasma of modified Dense Plasma Focus (DPF) [15] for nanofabrication of materials without dc biasing, heating of substrate or annealing. However, it was pointed out by some researchers that the ions produced in high temperature, high density and extremely non equilibrium plasma such as prevailing under fusion conditions are not useful for nanofabrication.

DPF device produces high density (10^{26} m^{-3}) and high temperature (1-2 KeV) pulsed plasma for a duration of ~ 100 ns which is a source of highly energetic ions, X-rays etc. The plasma produced under fusion conditions of high density, high temperature and strongly non equilibrium generates ions of material to be deposited in addition to ions of gas. High temperature and high density and strongly non-equilibrium plasma generating energetic ions, have been established by our group to have many applications in material processing such as phase change of materials [16-17], thin films deposition [18-19] and more recently fabrication of nanomaterials and nanostructures [20-22]. In this paper, we report the fabrication of silver using ions generated in modified device for two focused shots on silicon and glass substrate placed at a distance of 4.0 cm and 5.0 cm from the top of anode.

2. Experimental Details

A schematic arrangement of the experimental set up is shown in Figure 1. A modified DPF device consists of (i) rotary vacuum system and gas inlet (ii) plasma chamber and (iii) viewing port. It also consists of high voltage, low inductance capacitor (30 µF, 15 KV) with swinging cascade spark gap arrangement, triggering system and high voltage charger. For fabricating thins films and nanostructures an arrangement is made for inserting substrates from the top of chamber and the anode of the electrode assembly has been modified with a detachable arrangement on the top to host the cylindrical disc of the material to be deposited. A shutter is located above the anode and slightly below the substrates that protects the substrates from the impact of unfocused energetic ion. The axial movement of substrate holder, shutter and its distance from anode is controlled by a brass rod from the outside. A pure silver disc is made from silver rod and is fixed at top of anode. The silicon and glass substrates are cleaned and mounted on a substrate holder. The focus chamber is evacuated by a rotary pump and the chamber is admitted with argon gas through gas inlet. It was found earlier that if a device is operated at pressure of 80 Pa we obtain good focusing as can be seen on digital storage oscilloscope. The formation of plasma can be understood in a following manner: The capacitor is charged by a power supply and triggering circuit. The gas breakdown occurs between anode and cathode near the insulating sleeve. Image charges on the insulator sleeve initiate the discharge between the anode and the cathode forming weak current filaments leading to current density having an axially downward component.
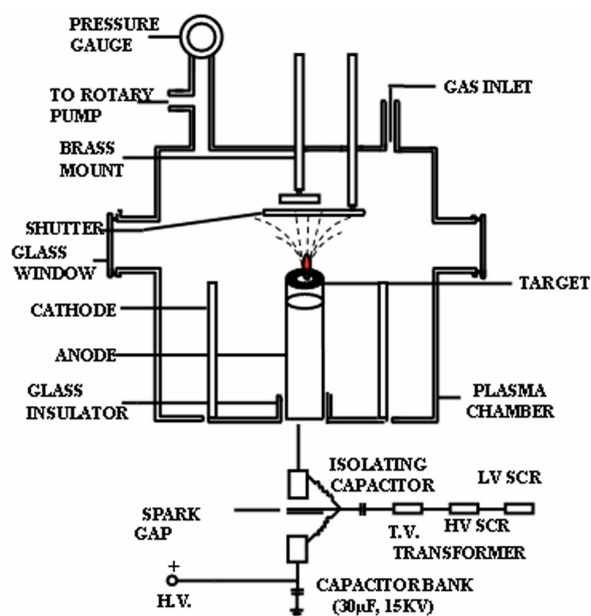

Figure. 1 Dense Plasma Focus device with its modifications.

The current in the anode creates an azimuthal magnetic field. The current filament then moves outwards due to radially outward Lorentz force arising due to axially downward component of current density and azimuthal magnetic field resulting in an inverse pinch phase. The current filament reaches the cathode due to this Lorentz force. As soon as the current sheath reaches the cathode the current filament has dominant radial component of current density. The radial component of current density and azimuthal magnetic field gives rise to axially upward component of Lorentz force which is responsible for axial phase of current sheath. This takes the current sheath towards the top of the electrode assembly. At the top of the anode, axially upward component of current density becomes dominant and this along with the azimuthal magnetic field give rise to a Lorentz force whose direction is radially inward causing the pinching of the plasma. The current sheath is accelerated towards the axis of the anode and plasma collapses to form a thin column of hot, dense plasma at the top of the anode. This is the focused phase having electron density of the order of 10^{26} m^{-3} and temperature 1-2 KeV. In this work we report the studies of silver nanostructures fabricated using two focused shots.

3. Results and Discussion
3.1 Structural Studies
The XRD spectrum is carried out using D8 Discover (with GADDS) with the CuKα radiation (λ = 1.54056A°) in 2θ ranging from 20° to 50°. The XRD pattern obtained for the silver deposited on any substrate placed either at 4.0 cm and 5.0 cm show identical behavior. Figure 2 shows the XRD pattern of silver deposited on silicon and glass substrate. Figure 2(a) show peaks at 2θ value of 38.1° and 44.5° corresponding to [hkl] plane of [111] and [200] respectively of fcc silver (JCPDS No. 4-783). The peak shown in figure 2(b) at 38.3°corresponds to [111] plane of silver on glass substrate.
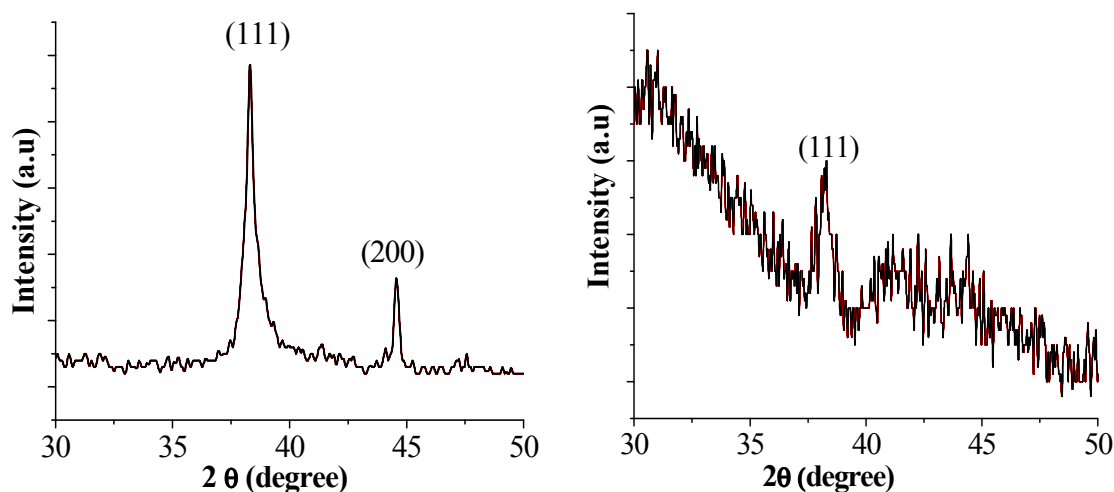

Figure 2. X-ray diffraction of grown silver nanostructures on (a) silicon and (b) glass substrate.

3.2 Surface Morphology
The surface morphology has been studied with the help of a CP-II atomic force microscope (AFM) in a non-contact mode. The AFM images were examined in terms of the surface roughness and the estimated height of silver nanostructures. AFM images of deposited silver nanostructures on silicon substrate placed at a distance of 4.0 cm and 5.0 cm from the top of the anode with two focused shot are shown in (a) and (b) of figure 3 respectively. The variation of mean height ($\overline{Z}$), peak to valley height (Rp-v), rms roughness (Rq), average roughness (Ra) and average height of deposited nanostructures with distance are given in table 1. The nanostructures formed are triangular in shape. This may be due

to the agglomeration of the particles forming different structures or this may be due to the condensation of ions on the substrates. The formation of nanostructures can be understood in the following manner. The highly energetic ions produced in the post focus phase reach the substrates, causing heating of the substrates prior to deposition. The high temperature argon plasma produces the silver ions. The silver ions are then mixed with argon ions moves vertically upwards in a fountain like structure and lose its energy to ultimately deposit on the substrate placed above the top of anode. The energetic ions hitting substrate surface may create nucleating centres and help in enhancing the adhesion of the deposited material to the substrate surface. The AFM of samples deposited on glass substrate shows cracks and pits. This may be due to the impact of highly energetic and high fluence ions that hit the substrate.
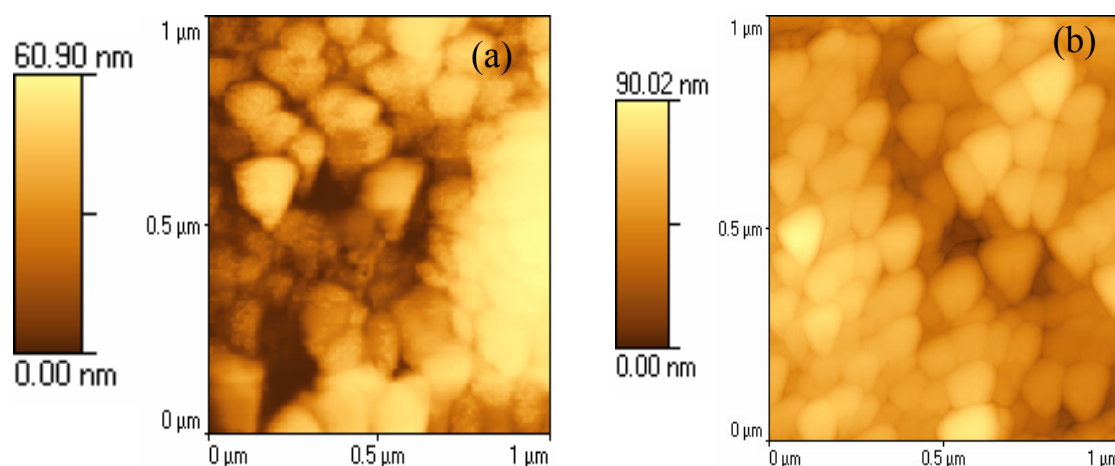

Figure 3. AFM image of silver nanostructures deposited on silicon placed at a distance of (a) 4.0 cm and (b) 5.0 cm from top of anode. The vertical bar on the left side of each image indicates height.

Table 1 Variation of $\overline{Z}$,Rp-v, Rq, Ra and Avg height with substrate placed from top of anode :

Substrates placed at (cm)	$\overline{Z}$ (nm)	Rp-v (nm)	Rq (nm)	Ra (nm)	Avg height (nm)
4.0	33	62	7	6	30
5.0	50	90	14	12	50

3.3 UV-Vis Spectra

In metal nanoparticles such as in silver, the conduction band and valence band overlap each other in which electrons move freely. These free electrons give rise to a surface plasmon resonance (SPR) absorption band, occurring due to the collective oscillation of electrons of silver nanoparticles in resonance with the light wave. The absorption spectrum of silver deposited on glass substrate is investigated. (a) and (b) of figure 4 shows the absorption spectra of silver nanostructures deposited on glass substrate placed at a distance of 4.0 cm and 5.0 cm from op of anode with two focused DPF shots respectively. The absorption peak at ~ 400 nm is observed for silver nanostructures deposited on glass substrates placed at a distance of 4 cm from top of anode is shown in (a) of figure 4. (b) of figure 4 corresponds to absorbance of silver deposited on glass substrate placed at 5 cm from top of anode and it shows a peak at 413 nm for silver nanostructures. This peak which is observed in the spectra is

attributed due to surface plasmon resonance (SPR). Silver nanostructures deposited at a distance of 5.0 cm from anode top on glass substrate display absorption peak at 413 nm, which is red-shifted about 13 nm as compared to the silver nanostructures deposited at 4.0 cm from anode top. Mulvaney [12] reports that the surface plasmon resonance (SPR) spectrum depends upon the refractive index of the surrounding medium, particle size, shape of particle and absorption substance of their surface. The red shifted in SPR is assigned due to bigger aspect ratio [23] or it can be due to increase in edge length and tip sharpness of silver nanoparticles.
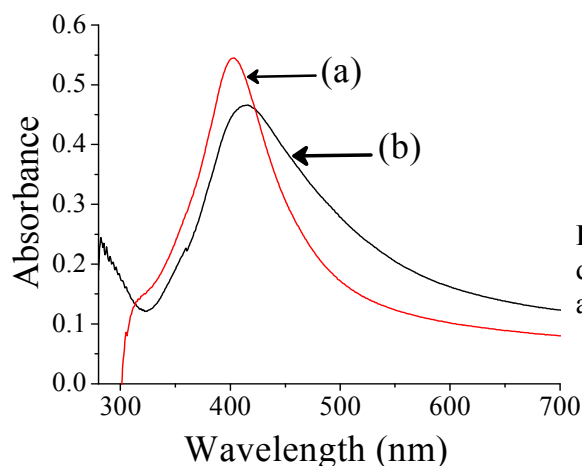

Figure 4. UV spectra of silver nanostructures deposited on glass placed at a distance of (a) 4.0 cm and (b) 5.0 cm from top of anode.

4. Conclusion
Highly energetic, high-fluence ion originated from the fully ionized gas and evaporated silver disc are deposited onto silicon and glass substrates without using any additional substrate biasing or heating which is most common in other devices. XRD shows the fcc planes corresponding to silver. AFM studies show the triangular shape like nanostructures. UV spectra show the peak which correspond to surface resonance plasmon.

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