Deposition and surface characterization of nanoparticles of zinc oxide using dense plasma focus device in nitrogen atmosphere

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Abstract: Nanoparticles of zinc oxide from zinc oxide pellets in the nitrogen plasma atmosphere are deposited on n and p type silicon substrates using Dense Plasma Focus device. The hot and dense nitrogen plasma formed during the focus phase ionizes the ZnO pellet, which then move upward in a fountain like shape and gets deposited on substrates which are placed above the top of the anode. Structural and surface properties of the deposited ZnO are investigated using X-ray diffraction and Atomic force microscope (AFM). X-ray spectra shows the diffraction plane (002) of ZnO nanoparticles deposited on Si with few shots in nitrogen atmosphere. AFM investigations revealed that there are nanoparticles of size between 15-80 nm on n-Si and p-Si substrates. The deposition on n-type Si is better than the p-type Si can be seen from AFM images, this may be due to different orientation of silicon.

1. Introduction
Nanofabrication of materials through plasma route is superior to other chemical and physical techniques. Recently, wide-band semiconductors have attracted great interest, because of their future possible applications in many areas, such as UV sensors, light-emitting diodes (LED's), laser diodes (LD's), and other high-speed high-power electronic devices. Zinc Oxide is a II-VI class semiconductor material that has been used in various areas, including phosphor, piezoelectric transducers, surface acoustic wave devices, gas sensors and varistors [1-2]. Zinc oxide with p-type conduction has recently attracted many researchers due to its potential applications in performing transparent p-ZnO/ n-ZnO homo-junctions LED’s. Such applications are difficult to achieve as ZnO occurs as n-type semiconductor in nature because of native
donors such as zinc interstitials and oxygen vacancies [3]. Zinc oxide is difficult to dope as p-type due to “self-compensation” effect caused by large background electron concentration [4]. Several p-type dopants like Li and group V elements nitrogen, phosphorous and arsenic have been used to prepare p-type zinc oxide. These elements are mainly used as they can generate acceptor state if incorporated on oxygen sites. Many researchers have used nitrogen as a dopant for ZnO by various techniques [5-7] and have demonstrated that nitrogen is considered to be a promising p-type dopant for ZnO. Besides these mono-doping studies, a few other groups proposed co-doping processes in which, a donor and an acceptor such as, gallium and nitrogen, nitrogen and oxygen, or other combinations [8-9] are used. An idea of cluster doping i.e., doping with even more partner atoms than in co-doping so, that acceptor formation can be optimized further was proposed by Wang and Zunger [10].

Bottom up approach for nanofabrication can be achieved by plasma methods in laboratory. Recently, it has been established that plasma aided nanofabrication [11-13] is among the best methods of deposition in which one makes use of the ions of material to be deposited. Several ion physical vapor deposition techniques for material processing are known as such, inductively coupled plasma magnetron sputtering (ICP-MS), high power impulse magnetron sputtering (HIPIMS) etc.. In most of the above mentioned methods, plasma produced is moderate density, moderate temperature and equilibrium. Ions under such plasmas conditions produce films or nanoparticles which require substrate heating, substrate biasing or annealing. Recently, it had been established in a series of papers that ions produced from hot, dense plasma similar to fusion conditions such as prevailing in DPF [14-15] can be used for phase changes [16-18], preparation of thin films [19-21] and more recently preparation of nanoparticles [11-12] as they do not require substrate heating, substrate biasing or annealing.

In the present work we have reported the use of high temperature (1-2 KeV) and high density (10^{26} m^{-3}) ions of nitrogen plasma in DPF device to produce ion of zinc, zinc oxide and oxygen using pellet of zinc oxide, placed above the top of the anode. These ions along with the nitrogen ions move upwards in a fountain like structure and condense on the n-Si (111) and p-Si (100) substrates which are placed at a distance of 5 cm above the anode. DPF device as has been earlier established [11, 12] for the preparation of nanoparticles have been used in the present study. DPF device used is 3.3 KJ Mather type device powered by 30 µF, 15 KV fast discharging energy storage Maxwell capacitor. We are reporting results for two focused shots on n and p type silicon substrate.

2. Experimental set-up

The DPF device used in the present study is as shown in figure 1. For deposition of nanoparticles of material the anode of the electrode assembly has been modified with a cylindrical detachable arrangement on the top so that the material in the form of cylindrical disc can fit into it. In the present work, pellets of ZnO having diameter equal to inner diameter of modified anode were made using zinc oxide powder. Zinc oxide pellet was then inserted at the top of the anode. Silicon substrates were cleaned with acetone and mounted on a substrate holder. Substrate holder is inserted from the top of the chamber and is mounted axially above the anode on an axially movable brass holder so that substrates can be adjusted to different heights above the
anode from outside the chamber. Shutter is placed between the substrates and the anode using movable brass holder so that the ions produced with no proper focusing do not hit the substrates.

Once, the good focusing is achieved which is evident as a spike in voltage probe signal in digital storage oscilloscope shutter is removed. Plasma chamber is evacuated using rotary pump and is filled with nitrogen gas. A 30 μF capacitor is charged to about 15 kV by a high voltage charger and is discharged through the electrode assembly with the help of fast switching system 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. 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 axially component 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 $10^{26} \text{m}^{-3}$ and temperature 1-2 KeV. ZnO pellet placed at the top of the modified anode is brought into ionized state by this high density and high temperature nitrogen plasma, producing Zinc Oxide, Zinc and Oxygen ions. All the three types of ions along with nitrogen ions move vertically upward in a fountain shape in post focus phase. These ions condense on the Si substrates placed above the top of the anode.
3. Results and Discussion
PW3710 diffractometer using CuKα radiation having wavelengths $\lambda_\text{CuKα} = 1.54056$ Å was utilized to investigate X-ray diffraction. The X-ray spectrum of zinc oxide nanoparticles obtained by few DPF shots was deposited on silicon substrate is as shown in figure 2. It shows peak at $2\theta = 34.3^\circ$ having c-axis orientation (002) of ZnO. No Zn or nitride peaks were found in XRD spectra. Guo [22] also had reported (002) plane of c-axis oriented ZnO films in N₂O plasma.

![Figure 2. X-ray diffraction of ZnO nanoparticles in nitrogen atmosphere on Si.](image)

The surface morphology was examined in terms of roughness and height of nanoparticles by using CP-II atomic force microscope (AFM). During the scanning, non-contact mode was used as a scan mode. The surface topography and the phase were obtained. From the phase image, phase shift of the oscillating cantilever relative to the driving signal is measured. The phase shift can be used to differentiate areas on a sample with such differing properties as friction, adhesion, and viscoelasticity.

![Figure 3. (a) 3D image, (b) Phase image of ZnO nanoparticles on n-Si.](image)

Figure 3 shows the micrographs of nanoparticles of zinc oxide in nitrogen ion atmosphere on n-Si (111) substrate. The surface topography and the phase were acquired by scanning 500 x 500 µm² area. 3D Atomic Force Microscope (AFM) image and phase image is shown in figure 2(a) and 2(b) respectively. We obtain from a typical horizontal line analysis using software of AFM, the Roughness average (Ra) to be 2.30 nm, maximum height of the profile above the mean line (Rp) to be 5.92 nm, mean of maximum height above mean line (Rpm) to be 4.02 nm, maximum peak-to-valley height (Rt) to be 12.61 nm and mean of peak-to-valley height (Rtm) to be 8.91 nm.
Figure 4 shows the micrographs of nanoparticles of zinc oxide in nitrogen ion atmosphere on p-Si (100) substrate. The surface topographies were acquired by scanning 1 x 1 µm² area. 3D Atomic Force Microscope (AFM) image and phase image is shown in figure 3(a) and 3(b) respectively. We obtain from a typical horizontal line analysis using the software of AFM, the Roughness average (Ra) to be 4.16 nm, maximum height of the profile above the mean line (Rp) to be 9.21 nm, mean of maximum height above mean line (Rpm) to be 7.13 nm, maximum peak-to-valley height (Rt) to be 22.97 nm and mean of peak-to-valley height (Rtm) to be 14.48 nm.

ZnO nanoparticles on n-Si (111) can be seen clearly in AFM images, but the nanoparticles deposited on p-Si (100) gets agglomerate. This may be due to the different orientation of n-Si (111) and p-Si (100).

4. Conclusion
Nanoparticles of Zinc Oxide have been successfully deposited, using dense plasma focus device. The DPF device is a source of highly energetic (1-2 KeV) and high fluence nitrogen ions which are used to deposit nanostructures of ZnO on n-Si (111) and p-Si (100) substrates. Thus, this study establishes that ZnO nanoparticles can be grown in nitrogen atmosphere as well. This opens possibility of doping ZnO with nitrogen producing p-type ZnO. The deposition on n-Si (111) is better than the p-Si (100) as can be seen from AFM images; this may be due to the orientation of n-Si (111) and p-Si (100).

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6. References
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