Plasma Route to Nanosciences and Nanotechnology Frontiers

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In this paper, I will discuss different routes to preparation of nanomaterials. The biological route provided in nature, chemical route and plasma route are indicated. The plasma route to prepare nanomaterials as compared to chemical route is highlighted. In particular, the plasma method, making use of Dense Plasma Focus device (DPF) to prepare nanomaterials is discussed. A 3.3 KJ, Mather type device modified with a detachable arrangement at the top of the anode where material to be deposited is fitted in the form of disc. The substrate holder is inserted from the top of the plasma chamber and different substrates at various distances each are placed at the top of the anode. The hot dense argon plasmas produced at the top of the anode produces the ions of target materials to be deposited. The argon ions along with fully ionized target atoms move upward in a fountain like structure. These ions are then deposited on different substrates. Nanoparticles of different optical, piezoelectric, semiconducting and magnetic materials etc. have been obtained. Some typical results of high resolution transmission electron microscopy (HRTEM) and atomic force microscopy (AFM) for characterization of fullerenes, lead zirconate titanate, aluminium, zinc oxide and cobalt are presented to establish the formation of nanoparticles.

Keywords: Plasma route, Nanofabrication, Nanoparticles, Nanostructures, Dense Plasma Focus Device, structural characterization

1. Introduction

The studies in Nanoscience and nanotechnology have received considerable importance due to its potential applications in sensors, robotics, image processing, biomaterials, conducting polymers, photonics, surface engineering, microelectronics, and metrology etc. A large variety of techniques are used for production of nanoparticles. Most of the earlier methods for production of nanoparticles fall into three categories viz. milling, vapor condensation and chemical synthesis. The oldest method used is milling or grinding and this process has produced nanoparticles for a long time even before the nano dimension of the particles was recognized. In vapor condensation, vaporization is followed by condensation and is used for making metallic and ceramic nanoparticles with better control over particles size and reduced contamination. Chemical synthesis is the most widely used method and involves growing nanoparticles in a liquid medium. Chemical synthesis permits the mixing at the molecular level and good chemical homogeneity, better control of the particle size, shape and size distribution can be achieved. Scaling up for the economical production of large quantity of material is easy for some but not for all. Milling or grinding are still used for materials where vaporization or chemical synthesis techniques cannot be used. Several other methods have been adopted for the manufacture of nanoparticles. These are (i) use of supercritical fluids with properties that are between those of fluids and gases as media for metal particle growth, (ii) electro deposit process, (iii) use of microwave and ultrasound and mimicking biology e.g., yeast cells make cadmium sulfide nanoparticles.

Biological route to nanoscience and nanotechnology is bottom-up processing technologies. Nanoscience is thought of as a physical science in today's world, but cell biology operates on exactly these length scales. Nature has made highly precise and functional nanostructures for billions of years such as DNA, proteins, membranes etc., but it is only since the 1980's that man has been able to manufacture such precise synthetic nanostructure at will. Nanostructures are made from thousands of atoms that are precisely defined in space. They have unlimited number of compositions, sizes, shapes and above all functionality.

Earlier methods for depositing thin films have been adopted for the preparation of nanoparticles in laboratory which are sol-gel, chemical vapor deposition (CVD) and

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physical vapor deposition (PVD. We can see from the biological route to the formation of nanoparticles, it follows bottom up approach. The bottom up approach for nanofabrication in laboratory can be achieved by plasma methods and the ion sources produced by plasma methods. More recently it has been established that plasma aided nanofabrication [1-4] is among the best methods of deposition in which one makes use of the ions of material to be deposited. There are several Ion PVD techniques in plasma based deposition process such as filtered cathodic arc deposition, self sustained sputtering, high power impulse magnetron sputtering (HPIMS), inductively coupled plasma magnetron sputtering (ICP-MS) and hollow cathode magnetron (HCM) sputtering, which are being used for nanoparticles deposition. In most of the above devices, the plasma produced is low density, low temperature or moderate density, moderate temperature, equilibrium or strongly non-equilibrium. Ion sources and ion beams from plasma sources is an important physical tool available for the design of nanostructures.

Earlier, it was general belief that the ions produced in high temperature, high density and strongly non-equilibrium plasma such as prevailing under fusion conditions are not useful for material processing to achieve phase changes, thin film preparation. It has been established in a series of papers that ions produced from hot dense plasma similar to fusion conditions such as the one prevailing in Dense Plasma Focus device (DPF) [5,6] can be used for phase changes [7-11] and preparation of thin films [12-14]. In the present paper the results of nanoparticles or nanostructures obtained from one focused shot of DPF device have been reported. The duration of one focused shot is about 100 ns and it deposits 40-50 nm of the target material onto the substrate at a pressure of 80 Pa. The target material is small circular disc of diameter equal to inner diameter of anode. In this device the substrate does not require dc biasing or heating to substrate and chamber need not be at very high vacuum. The nanoparticles were not required to be annealed after deposition. We are briefly reporting the results of nanoparticles deposition of fullerene, PZT, Al, ZnO and cobalt.

2. Experimental set-up

The DPF device used for preparation of nanoparticles in the present work is a 3.3 KJ Mather type device and is shown in Fig.1. The anode is modified from conventional DPF device for preparation of nanoparticles. Modified DPF device consists of (i) electrode assembly with a modified anode in which a disc whose material to be deposited is fitted at the top of the anode and enclosed in plasma focus chamber, (ii) capacitor with switching cascade spark gap arrangement, (iii) triggering electronics system to activate the spark gap assembly and (iv) an arrangement for inserting the substrate on which the nanoparticles are to be deposited. The plasma focus chamber consists essentially of a central hollow cylindrical copper anode.

For the preparation of nanoparticles of any material, the top of the central anode which is detachable is fitted with material to be deposited in the form of a circular disc. The modified anode is surrounded by six symmetrically placed solid copper cathode rods arranged in a squirrel cage like structure. There is an insulator sleeve made of glass between cathode and anode which shapes the plasma

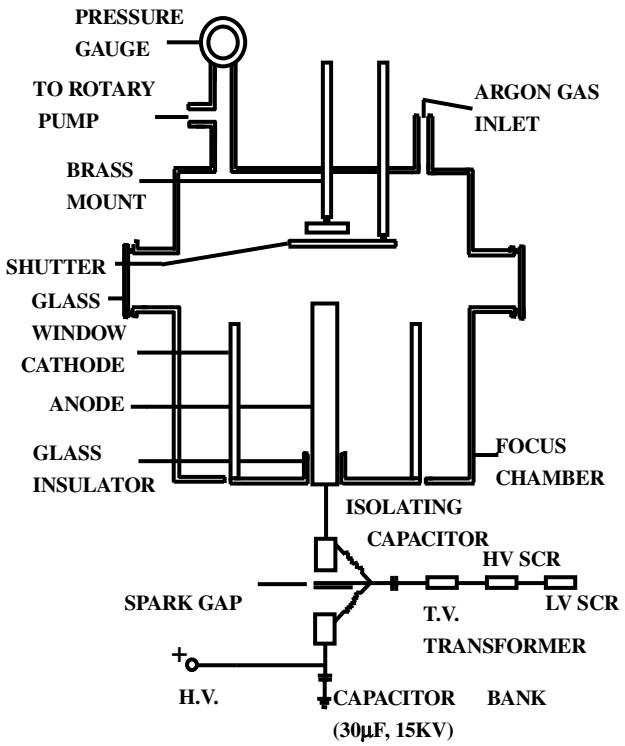

Fig.1. Dense Plasma Focus device with its modifications

sheath during initial breakdown. The capacitor bank that energizes the DPF is a single 30 μF, 15 KV oil filled Maxwell capacitor. A movable brass holder is inserted from the top of the chamber so that the substrates can be adjusted axially at any height above the top of the anode. A shutter is also introduced in between the substrates and the top of the anode using a movable brass holder. The vacuum in the plasma chamber is obtained by a rotary

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pump. Argon gas is filled in the plasma chamber in the present case through the gas inlet and is flushed several times to minimize the impure gas in the chamber. The capacitor is charged to 15 KV from a high voltage power supply and is allowed to discharge 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 cathode forming weak current filaments having an axially downward component. The current in anode creates an azimuthal magnetic field. The current filaments then move 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 the 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 upward current density along with the azimuthal magnetic field gives 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 anode and plasma collapses to form a thin column of hot, dense plasma at the top of the anode. This is the focus phase in which the electron density is of the order of 10^{26} m^{-3} and temperature of the order of 1-2 KeV. This focused hot plasma has the ions of inert gas and also produces the fully ionized ions of target material which move vertically upward in a fountain like structure in the post focus phase. Good focusing is indicated by a sharp peak in the voltage signal which is recorded on an oscilloscope using a voltage probe. Until a good focusing is attained, the shutter is placed between the top of anode and the substrates to prevent lower fluence ions not to reach the substrates. The highly energetic, high fluence argon ions produced with good focusing along with material ions move upward in a fountain like structure and get deposited on the substrates.

3. Results and Discussion

Nanoparticles have been prepared by optimizing the distance between the anode and the substrate, the pressure of the gas in the plasma chamber, the charging voltage applied to the capacitor and the number of shots. The DPF device has been used to make nanoparticles of different material and in particular the results of fullerene, lead zirconate titanate (PZT), zinc oxide, aluminium and cobalt are presented here. Fig.2. shows HRTEM of fullerenes having grain size of the order of 0.7 nm [13].

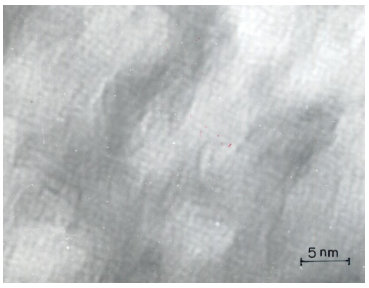

Fig.2. HRTEM of Fullerene

HRTEM micrograph of nanoparticles of PZT is shown in Fig. 3 [15]. The average size of nanoparticles is of the order of 0.5 nm.

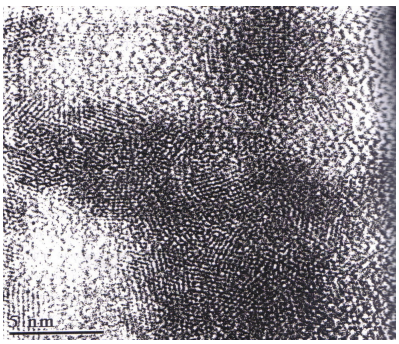

Fig.3. HRTEM of PZT

The atomic force microscope (AFM) image of aluminium nanoparticles [16] is shown in Fig. 4. The typical line analysis of AFM image of aluminium nanoparticles gives a roughness average, maximum height of the profile above the mean line, mean of maximum height above mean line, maximum peak-to-valley height and mean of peak-to-valley height to be 7.52 nm, 22.70 nm, 10.56 nm, 42.45 nm and 23.17 nm respectively.

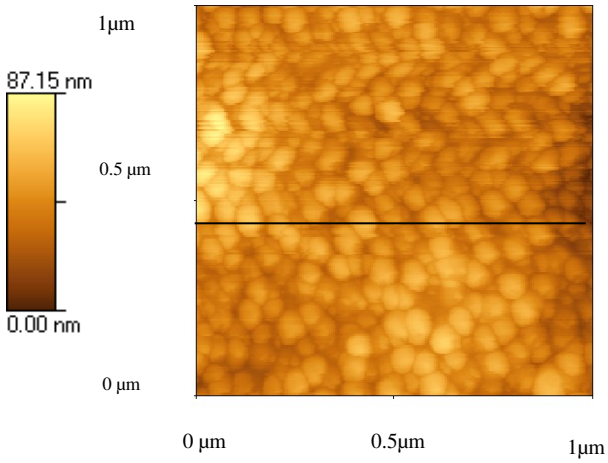

Fig.4. AFM image of aluminium

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The AFM image of zinc oxide nanoparticles [17] is shown in Fig. 5.

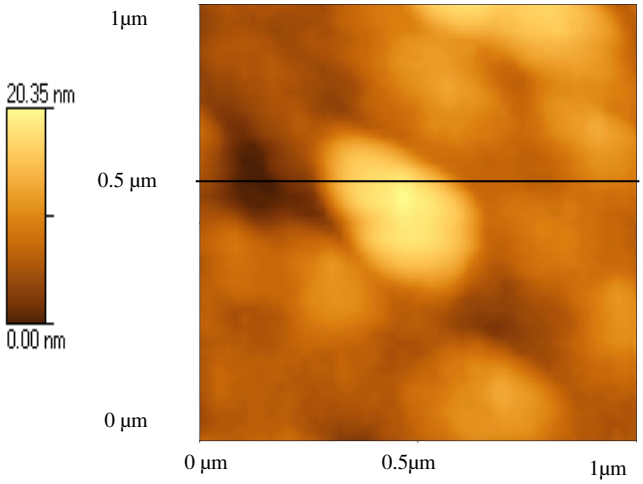

Fig.5. AFM image of zinc oxide nanoparticles

From the line analysis of AFM image of ZnO nanoparticles, we have found the roughness average (Ra), maximum height of the profile above the mean line (Rp), mean of maximum height above mean line (Rpm), maximum peak-to-valley height (Rt) and mean of peak-to-valley height (Rtm) to be 3.98 nm, 9.34 nm, 3.57 nm, 15.98 nm and 5.97 nm respectively. The AFM image of cobalt nanoparticles [18] is shown in Fig.6. From a typical line analysis, we have found roughness average, maximum height of the profile above the mean

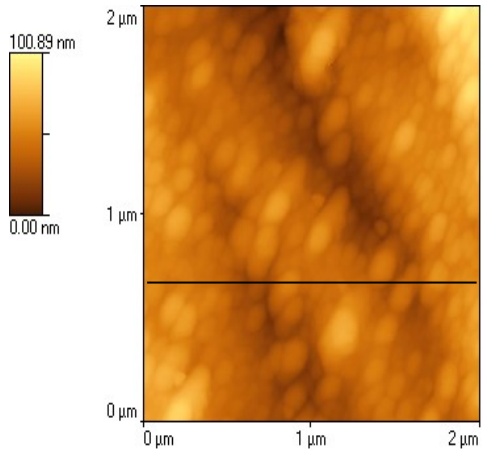

Fig.6. AFM image of cobalt nanoparticles

line, mean of maximum height above mean line, maximum peak-to-valley height and mean of peak-to-valley height to be 10.55 nm, 23.13 nm, 12.89 nm, 55.06 nm and 25.65 nm respectively. Thus, we have deposited nanoparticles of fullerene, PZT, ZnO, Al and cobalt using DPF device. Here we follow bottom up approach as is prevalent in biological processes in nature. DPF device is much better as compared to other techniques for depositing nanoparticles and nano-phased films.

The methods for depositing thin films which have been adopted for the preparation of nanoparticles in laboratory which are sol-gel, chemical vapor deposition (CVD) and physical vapor deposition (PVD). Sol-gel process is a wet chemical technique with drying and thermal treatment subsequently for the fabrication of material with enhanced mechanical properties. In this method, we have better control of stoichiometry, purity and homogeneity of films for electronic and optical applications. However, this method may be used only for polymeric materials and substrates should be water insoluble. In CVD process the substrate is exposed to one or more volatile precursors which react and decompose on the substrate surface to produce the desired deposit. Volatile byproduct are also produced which can be removed by gas flow through the reaction chamber. Many different forms of CVD have been used depending on operating pressure. It has been found that the enhancement in the rate of deposition in CVD process can be achieved by plasma methods such as RF or microwave assisted plasma. Atomic layer CVD is used to deposits successive layers of different substances producing layered crystalline films. PVD process is achieved either in evaporative deposition in which material is heated to a high vapor pressure by electrically resistive heating in low vacuum or electron beam PVD in which material to be deposited is heated to a high vapor pressure by electron bombardment in high vacuum. In PVD one deposits thin films by condensation in vaporized form. Some other modified PVD methods are (i) sputter deposition, (ii) cathodic arc deposition and (iii) pulsed laser deposition.

Glow discharges and in particular the magnetron sputtering discharge have low deposition rate and the ion chemistry is usually dominated by the ions of the inert sputtering gas while ions of the sputtered material are rare. There is an upper limit to the power that can be delivered to the target. High power impulse magnetron sputtering (HPIMS) have plasma densities of the order of ~ 10^{19} m^{-3} However, deposition rate is low. Filtered cathodic arc deposition suffers from generation of macroparticles in the range of 0.01-10 µm (droplets) emitted during the explosion of microprotrusions (asperities) in the cathode spot which are incorporated into the growing film forming voids and large scale defects. In Pulsed Laser Deposition technique, films of larger sizes and thickness and without particulates (droplets) cannot be prepared. The films can be directionally dependent due to different temperatures in central and outer parts of the plume. PLD technique is

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also an expensive technique as it uses costly solid state or excimer lasers. Most of these methods require either bias voltage or heating of the substrate.

In most of the above devices, the plasma produced is low density, low temperature or moderate density, moderate temperature, equilibrium or strongly non-equilibrium. Ion sources and ion beams from plasma sources is an important physical tool available for the design of nanostructures. It has been general belief that ions produced in high temperature, high density and strongly non-equilibrium plasma such as prevailing under fusion conditions are not useful for the preparation of nanoparticles. In this paper we have shown/ established that even one focused shot of DPF device having duration of 100 ns allows deposition of nanostructures and nanoparticles onto the substrate. In this technique we require very small quantity of starting material and a vacuum of the order of 80 Pa only as compared to other techniques which require ultra high vacuum. The DPF device does not require any dc biasing or heating of the substrate. The adhesion of the material depends on the nature of substrate used. The nanoparticles and nanostructures are free from particulate material which is a cause of concern in Filtered cathodic arc and PLD techniques. Moreover, DPF device is simple and cost effective as compared to other plasma deposition techniques.

4. Conclusion

It has been demonstrated that ions produced with the help of high density, high temperature and strongly non-equilibrium plasma such as the one available in DPF device can be used in the preparation of nanoparticles or nanostructures of a variety of materials without heating or biasing of the substrate and without annealing the nanoparticles with laser, ion beam or thermally. DPF device does not have the major disadvantages of other methods like particulate matter in the film, ultra high vacuum, substrate biasing, substrate heating and annealing etc.

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