# Characterization of spherical tin nanoparticles with melted inner layer synthesized using dc magnetron sputtering plasma

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**Abstract:** The importance of nanoparticles is rapidly increasing in recent years with raise in its application areas. The quest for latest advancements in synthesizing tin (Sn) nanoparticles are addressed in this study by using dc magnetron sputtering process; wherein spherical Sn particles, which had melted inner layers covered with outer layers, were produced. These observations play a vital role in developing phase changing materials for thermal energy storage applications. The sizes of synthesized particles ranged between 100 and 200 nm.

**Keywords:** plasma synthesis, dc magnetron sputtering, tin, nanoparticles, melted inner layer.

## 1. Introduction

The importance of nanoparticles is rapidly increasing in recent years because of its diverse applications across various disciplines of science and technology. Hence, there is a serious quest for latest advancements in nanoparticle synthesis technologies. Plasma-assisted nanoparticles synthesis being one of the promising techniques with its unique advantages can be very useful in developing various types of nanoparticles. dc magnetron sputtering coupled with rf plasma gives flexibility in controlling particle growth [1] and heating. The current research is focussing on the synthesis methodology for developing spherical Sn particles with a melted inner layer that is covered by an oxidized layer. Sn nanoparticles application areas includes gas sensing applications. The nanosized materials are well known for their size dependent properties [2] and the higher surface to volume ratios [3]. The outer layer observed to be $SnO_2$ from the stoichiometric ratio (~ 1.8 - 2.5) which are closely matching with the literature [4]. Modified forms of tin particles are also used in the battery applications [5]. Sn material is of interest in developing phase changing materials because of its low melting point of ~ 231.9 ºC, that are discussed in the literature with silica as the shell material [6].

In this research, the synthesis process, and the challenges for obtaining Sn nanomaterials with melted inner layer are discussed. The measured details from TEM and EDS give the better understanding of the difference in oxidation, melting of tin particle inner layer and outer layer. Also, the particle size can be observed in the experiments with the change in the keeping/heating time.

## 2. Experimental Methods and Materials

The series of process steps in the synthesis were the preparation of the work pieces (for the collection), the vacuum preparation with a pressure below $4x10^{-6}$ Torr, adjusting the working pressure (~ 40 to 130 Pa), sputtering of a tin target, heating (keeping) using an rf plasma, and collecting synthesized particles. A dc magnetron sputtering source was placed at the top of a vacuum chamber. Argon (Ar) gas was used for the sputtering discharge in this research. A ring electrode, which was connected to an rf power supply at 13.56 MHz, was installed at the bottom of the vacuum chamber, and it was used for producing capacitively coupled rf plasma. A positively biased electrode was placed inside the ring rf electrode, and it was used for collecting nanoparticles. We put aluminium (Al) work pieces and copper grits for the TEM observation on the positively biased electrode for collecting nanoparticles. The sputtering duration was between 60 and 120 s based on the preliminary experimental observations. The heating using the rf plasma for 180-300 s was provided for the particle growth and the possible melting of Sn particles. The positive bias voltage of 70 V was effective for collecting nanoparticles onto the work piece and the TEM grit. The collected particles were characterized using scanning electron microscope (SEM), transmission electron microscope (TEM), and energy dispersive spectroscopy (EDSx). The sizes of particles were analyzed using the open-source software Image J.

## 3. Results and Discussion

The observations made on the data obtained using SEM, TEM, and EDSx are discussed in this section. The broad of experimental conditions and the particle sizes are shown in Table 1. From the particle size measurements, it can be inferred that the growth of the particle size has direct relation with the heating (keeping) time. It can be seen in Table 1 that the average (mean) particle size at the keeping time of 300 s (No. 7) is remarkably larger than that at 180 s.

Table 1. Experimental conditions and particle sizes

| Exp No. | Voltage (V) | Keeping time (s) | Pressure (Pa) | Particle Size (nm) | | |
|---|---|---|---|---|---|---|
| | | | | Max | Min | Mean |
| 1 | 280 | 180 | 90 | 222 | 86 | 136 |
| 2 | 280 | 180 | 70 | 90 | 53 | 70 |
| 3 | 280 | 180 | 70 | 220 | 64 | 152 |
| 4 | 240 | 180 | 90 | 235 | 87 | 137 |
| 5 | 280 | 240 | 75 | 229 | 60 | 117 |
| 6 | 300 | 180 | 70 | 341 | 54 | 128 |
| 7 | 300 | 300 | 90 | 385 | 270 | 345 |
| Sputtering time was 60 - 120 s.<br>The rf power was 40 W (50 W for No.4).<br>Voltage means the dc magnetron sputtering voltage | | | | | | |

Surface morphology and different types of particles with different sizes are observed in the SEM image shown in Fig. 1(b). There is also difference in the darkness of the transient region from the inner to outer layers and the

porosity in the outer layer. From the TEM observations, it is evident that the inner layer has less efficient transmission of the electron beam and it has a shape close to a complete sphere without porosity. This suggests that the material of the inner layer is metallic Sn, and the Sn particles were melted when they were stored in the rf plasma. There are particles in TEM data without dark inner layer (Fig. 1(a)), which is possibly the challenge in obtaining uniform heating distribution of particles over the rf plasma. Particles of different sizes were expected to be formed during the particle growth after sputtering.

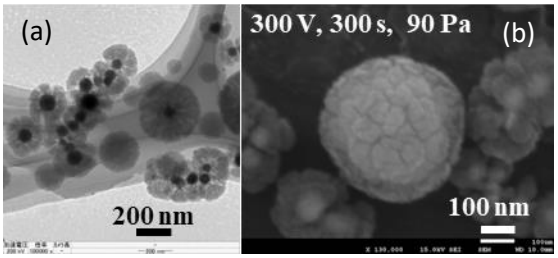


Figure 1. (a) TEM and (b) SEM images of nanoparticles at experimental condition 7.

Nanoparticles observed at condition 3 can be seen in Fig. 2, where in different surface morphologies and sizes are observed. Likewise, various sizes of nanoparticles are observed at different experimental conditions.

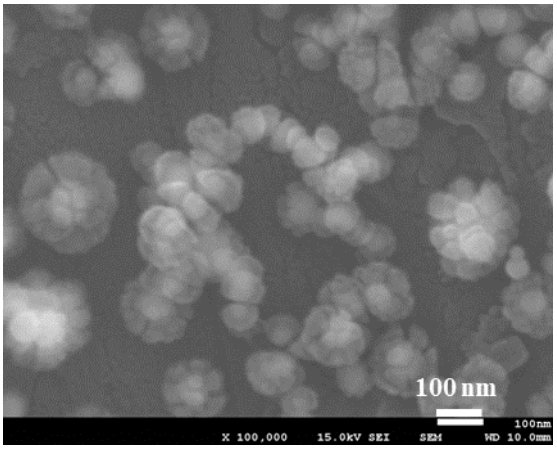


Figure 2. SEM image of nanoparticles at condition 3.

The melted nature of the inner layer can be further understood in the EDSx plot shown in Fig. 3. Both the outer and inner layers of the synthesized Sn particles are depicted in the plot. There is a clear difference in the oxygen and tin peaks for inner and outer layers. Further the stoichiometric ratios of oxygen to tin of the outer layer are closely analogous to $SnO_2$. The oxidation is possibly caused by impurity oxygen in the plasma, but a more likely oxidation process is the reaction when the vacuum chamber is exposure to air. In addition, if it is $SnO_2$ covered on Sn, it may be useful thermal and sensing applications.

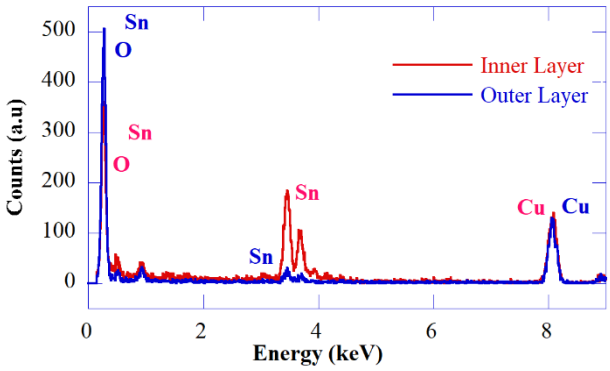


Figure 3. EDSx plots of the elements at experimental condition 7.

There are some challenges in obtaining homogeneous nanoparticles with melted inner layer, such as collection and temperature distribution in the rf plasma. Also, the particles stored at a long distance from the rf electrode are expected to have less efficient heating. Addressing this temperature distribution problem could be favourable to utilize the methods for developing phase change materials.

## 4. Conclusions

Tin nanoparticles with melted inner layer covered by oxidized outer layer were synthesized and characterized. The sizes of the particles ranged between 100 and 300 nm. The oxidation was found to be predominant in the outer layer than the inner layer. The process method can be used for developing tin particles covered with a $SnO_2$ layer. Also, the melted inner layer having close relevance with developing phase changing materials to be used in thermal energy storage applications; even to develop in combination with other materials with different melting point.

## 5. References

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