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# Investigation of the Properties of Molybdenum Nanocube Crystals Deposited by Dc Sputtering

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Cubic molybdenum (Mo) nanocubes were deposited on a silicon substrate via dc sputtering. This method has been widely used to prepare the thin films containing the crystalline nanostructures. We used this approach to deposition and after that, the characterization of Mo nanocubes. Formation of these cubes was investigated by atomic force microscopy, X-ray diffractometry and four point probes, respectively. First, the mean sizes of the molybdenum cubic nanoparticles were studied under different Mo film thicknesses of 50, 80, 110, and 140 nm. Structural characterizations indicate that the as-deposited Mo nanocubes have different side-length and their distribution over the surface has been measured, separately. In the next step, according to the X-ray diffractometry, Mo crystallites were all along the (110) crystal planes of cubic structure. Finally, electrical characterizations reported that at a deposition power of 54 W, our samples exhibit an electrical resistivity, in the range of $0.92 \times 10^{-4}$ Ω cm to $0.58 \times 10^{-4}$ Ω cm.

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## 1. Introduction

Nanomaterials exhibit unique properties which are interesting in technology. Nanoparticles are one of the main important topics in nanosciences, because of their size and also increased surface to volume ratio. Among these materials, metallic nanoparticles have found many technological applications. Here, we focused on cubic Mo nanoparticles. Molybdenum finds uses in a broad range of fundamental to industrial applications. This metal is one of the key transition metals which offer a wide range of attractive aspects. It is silvery-white in appearance, refractory metal [1] with important chemical and physical properties. Chemically, in most environments it has very good stability [2]. Mo and its compounds have been extensively used in chemical, lubricant and petroleum industries for different purposes as a lubricant or catalyst [3], or in the production of polymers and plastics [4].

Physically it is important because of its mechanical, electrical and thermal properties. Mo is very hard [5], resistant to high loads and has high (specific) elastic modulus [6]. This characteristic makes it attractive for applications that require good stiffness (greater than that of steel) along with low weight. When it is alloyed with steel, improves the corrosion resistance [7]. Molybdenum has good electrical conductivity [8]. It has been also used as arc resistant electric contacts [9], electrodes [10], and thermocouple sheath or as a filament substance into lighting technology or in other high performance electrical and electronic applications [11].

Thermal properties of this metal make it unique among others. It exhibits very high melting point (the sixth between all other elements) [12], low coefficient of thermal expansion (less than that of most steels and the lowest in comparison with that of other engineering materials) and relatively high thermal conductivity [13] which exceeds that of many other elements. Important aforementioned characteristics of molybdenum extended its potentiality to nuclear energy applications, fusion devices and tokomaks [14].

Different physical or chemical methods for preparation of Mo thin films in the literatures have been used and reported, such as dc/rf magnetron sputtering [9, 15–18], ion beam sputtering (IBS) [19], or laser assisted methods such as pulsed laser deposition [20], laser ablation deposition [21, 22] or laser photolytic deposition [23]. Steered arc deposition (SAD) [24], thermal evaporation [25] or electron beam evaporation [9, 16, 24, 26, 27] and finally chemical methods like CVD or low pressure chemical vapor deposition (LPCVD) [28] also have been reported.

The paper is organized as follows. So far, most important properties of Mo along with applications and different preparation methods of Mo thin films were reviewed, briefly. In next section (experimental), the deposition conditions and key parameters, along with structural, morphological and electrical characterization are presented. The results and discussion are given in Sect. 3. Finally, conclusions are summarized in the last section.

## 2. Experimental section

### 2.1. Deposition conditions and parameters

The Mo thin films, containing the crystalline nanocubes were deposited on silicon substrates in a typical dc sputtering system (EDS Model 160) using Mo target (99.5%) in pure Ar gas medium. It has a high vacuum stainless steel chamber of 110 L in volume, two view ports and twelve feed through bores. The sputtering chamber

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is equipped with diffusion and rotary pumps with a base pressure of $4 \times 10^{-5}$ mbar. The substrates were washed, cleaned ultrasonically and dried progressively, before to be introduced in the chamber. Deposition parameters of the experiment are summarized in Table I.

TABLE I

The deposition conditions of Mo thin films.

| conditions and parameters | values |
|---|---|
| target, diameter | Mo (99.5%), 90 mm |
| substrate | Si, 1 cm $\times$ 1 cm |
| target-substrate distance [cm] | 7 |
| base pressure [mbar] | $4 \times 10^{-5}$ |
| working gas, pressure [mbar] | Ar, $2 \times 10^{-2}$ |
| voltage [V] | 300 |
| current [mA] | 180 |
| sputtering power [W] | 54 |
| film thickness [nm] | 50, 80, 110, 140 |
| samples label # | 1-2-3-4 |

To illustrate the effect of the thin film thickness, four Mo films with thicknesses of 50, 80, 110, and 140 nm were deposited on the substrates with sample label #1 (50 nm) to 4 (140 nm). The thickness of the films and the rate of deposition were controlled using the quartz crystal monitor in the chamber.

### 2.2. *Characterizations*

The samples were characterized by X-ray diffraction (XRD), four point probe (FPP) and atomic force microscopy (AFM). Analysis of the crystalline structures was performed by XRD diffractometer (Philips PW 3710) with wavelength of Cu $K_\alpha$ radiation in $2\theta$ range from 30° to 60° by 0.5° min$^{-1}$ steps. The surface morphology of the samples was examined by an atomic force microscope (AFM) (Park Scientific Instruments, Auto probe CP) operated in contact mode. The scanning area was set at 2 $\mu$m $\times$ 2 $\mu$m.

## 3. Results and discussion

The results of our structural, electrical and morphological studies are discussed in this section. Figure 1, in the center, gives X-ray diffraction of the samples #1–4. It reveals that the crystallites of Mo films are all oriented along the (110) direction of cubic crystal structure, with a peak at around $2\theta = 40°$. Accordingly, we can analyze the structure of the films by determining the full width at half maximum (FWHM) as a measure of crystallite size. We can calculate the crystallinity of the Mo films using FWHM (Fig. 1, center) of the related (110) X-ray peaks by considering Scherrer's equation. The grains size was measured in the range of 4–9 nm for the samples. Crystallinity has been increased by the film thickness (increasing the peak intensity).

Figure 1 also shows two-dimensional images of the entire as-deposited Mo thin films on silicon surface and change in the surface morphology. The values of root mean square and average roughness of the samples were measured and it was increased by increase in the film thickness. As we can see from the figure, the surface is covered by cubic nanoparticles crystals.

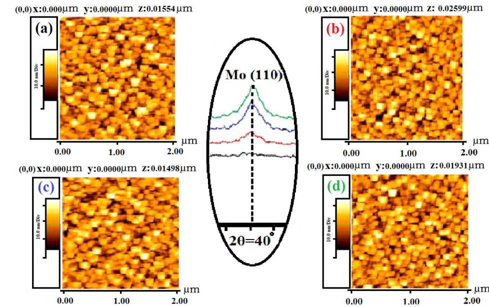


Fig. 1. XRD patterns (center) and 2D-AFM micrographs of the samples with different thicknesses of molybdenum films containing the cubes: (a) 50 nm, (b) 80 nm, (c) 110 nm, (d) 140 nm.

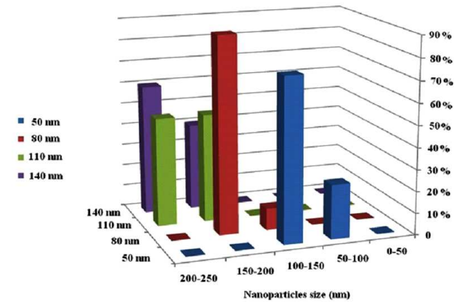


Fig. 2. Percentage from total number of cubic nanoparticles versus their side length (nanoparticle size) in nanometer according to the film thicknesses [nm].

The side length of the cubes was also measured for all the four samples and their distribution over the surface is presented in Fig. 2.

In the first sample (50 nm in thickness, shown with blue color in the first front row), we measured the side length of cubes, over the surface. Although we can find the cubes with a side length between 50 and 100 nm, but, approximately more than 70% of the cubes have a side length in the range of 100–150 nm. By increasing the film thickness, to 80 nm, this maximum range varies from 150–200 (brown color) to 200–250 nm for the cubes of third and forth samples (110, 140 nm), shown in green (third row) and in purpule (last backward row). In other words, to having cubes with a side length less than 100 nm, a thickness of 50 nm or less is appropriate.

Electrical characterization of the samples was also conducted and sheet resistance values were measured by four point probe technique. The deposited Mo layers exhibited a low resistivity. The lowest resistivity value, which we found for our Mo films, was 58 $\mu\Omega$ cm.

## 4. Conclusions

In this paper, we prepared Mo nanocube crystals with different side lengths using dc sputtering technique. The effect of film thicknesses (50, 80, 110 and 140 nm) on the structural, morphological and electrical properties of the films and formed nanocubes with different side lengths was investigated. The experiments demonstrated that:

1) DC sputtering with a 54 W power at the above mentioned conditions can produce Mo nanocube crystals with a side length in the range of 50–250 nm for the film thickness in the range of 50–140 nm.

2) The morphology of molybdenum film surface and also the nanocube side length in the dc sputtering method proposed here to growth and preparation of nanocubes such as other techniques were found to be dependent on the film thickness. In lower thicknesses, we can find a side length of 50–100 nm, whereas must of the cubes length are 100–150 nm for the first sample and 150–250 nm for the last ones. By increasing the film thickness, the cube percentage with a side length in the range of 100–150 nm and 150–200 nm decreases.

3) The deposited Mo layers exhibited a resistivity value of 58–92 $\mu\Omega$ cm.

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