Chapter

Bottom-Up and Top-Down Approaches for MgO

Jitendra Pal Singh, Manish Kumar, Aditya Sharma, Ganesh Pandey, Keun Hwa Chae and Sangsul Lee

Abstract

In this chapter, we present an overview of synthesis of MgO nanoparticles and thin films by using top-down and bottom-up approaches. The bottom-up approaches are generally utilized to grow nanoparticles by the methods that involve chemical reactions. Sometimes, methods based on these reactions are also able to grow thin films. The top-down approaches are preferred for growing thin films where bulk material is used for depositions. The methods, which are frequently used, are radio frequency sputtering, pulsed lased deposition, and molecular beam epitaxy and e-beam evaporation. Sometimes, methods like mechanical milling and high energy ball milling are used to grow nanoparticles.

Keywords: MgO, bottom-up approaches, top-down approaches

1. Introduction

Nanoparticles and thin films are very common form of materials for utilization in different applications [1–4]. Synthesis approaches play vital role to determine characteristics of nanoparticles [5] and thin films [6]. Thus, a number of methods are being developed to synthesize either nanoparticles [7–9] or thin films [10–12]. The motive behind to explore numerous methods is to look for reproducibility and cost effectiveness in terms of industrial utilization [13, 14]. Researchers are also working to get deep insights of involved phenomena during growth which persists a way to optimize for particular application [15–18]. The factors, which are considered during nanoparticle growth, are size [19], shape [20, 21] and size distribution [22, 23]. In case of thin films, these factors are nature of growth, morphology, stress, strain developed across films substrate interface [24–26].

While growing nanoparticles, one need to take care annealing treatment [27, 28] and stoichiometry [29, 30], however, process is rather typical in case of thin film technology. Choice of substrate [31], annealing temperature [32, 33], base pressure [34], target to substrate distance [35], deposition pressure [36, 37] and nature of gas during growth determine the nature of film [38]. Textured of grown thin film [39], stoichiometry [40] and nature of surface [41, 42] are another important parameter, which are considered during deposition. Thus, keeping in mind the necessity and challenges in the synthesis, synthesis approaches for growing nanoparticles and thin films are discussed by taking a simple inorganic system. However, magnesium oxide is known from long time [43] but recent advances in application of this material motivated us to discuss these approaches for MgO [44]. In **Table 1**, a summary of properties of MgO are depicted [45–47].

While keeping in mind the importance of this material, we attempt to give an overview of synthesis of MgO nanoparticle and thin film. To grow nanoparticles, two kinds of approaches are used: (1) bottom-up approach and (2) top-down approach [48, 49]. These approaches are explained on the basis of following schematic diagram. In general, bottom-up approach is meant by synthesis of nanoparticles by means of chemical reactions among the atoms/ions/molecules (**Figure 1a**). Whereas top-down involves the mechanical methods to crush/breaking of bulk into several parts to form nanoparticles (**Figure 1b**). In the next section both kind of approaches for growth of MgO nanoparticles and thin films are grown.

Properties/applications	Bulk [43, 45]	Nanoparticles [44]	Thin films [45]
Crystallite structure	Rocksalt	Rocksalt	Rocksalt
Lattice parameter (Å)	4.214	4.128	4.22
Optical band-gap (eV)	7.6	4–5	4–5

Table 1.
Properties and applications of MgO bulk, nanoparticles and thin films.

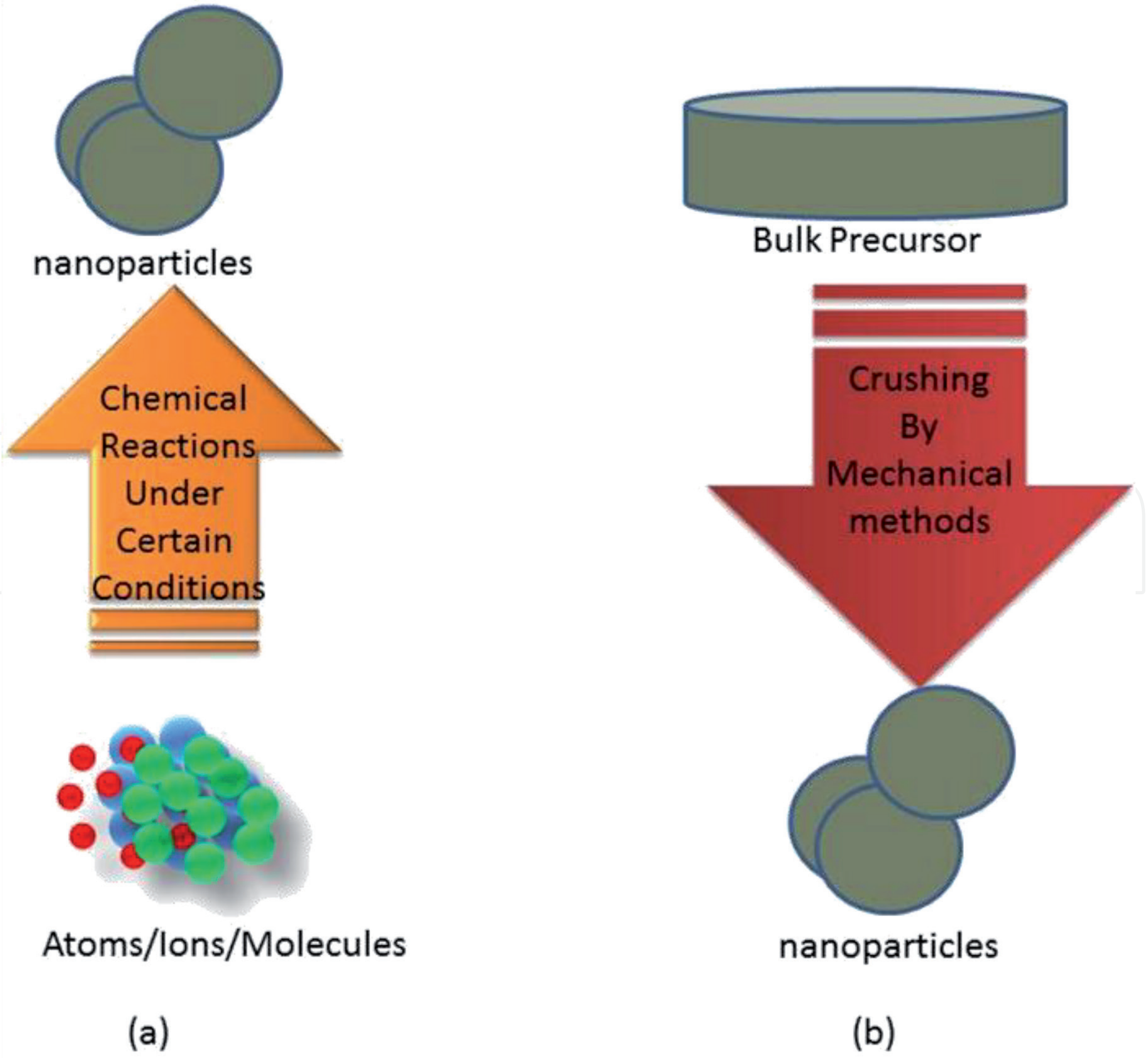

Figure 1.
Synthesis approaches for nanoparticles (a) bottom-up and (b) top-down approaches.

2. Bottom-up approaches

2.1 MgO nanoparticles

To initiate chemical reaction among the involved atoms/ions/molecules certain salts are taken as starting materials. These salts are mixed with each other to form a homogeneous solution along with a suitable chelating agent. Control of nature of solution also plays important role during synthesis process [50]. Thus, various methods are being developed by researchers to minimize annealing treatment, nature of chelating agent, pH value of solution. Some of these methods are depicted here.

Combustion synthesis is well known phenomena to synthesize nanomaterials of different kinds in its different variance [51, 52]. Most of the study utilizes solution combustion process for synthesizing nanoparticles. Typically, this method involves an oxidizer and fuel to initiate the reaction [53–55]. The most common oxidizers are metal nitrate/hydrates, ammonium nitrate and nitric acid. However, Urea, Glycine, Sucrose, Glucose, Citric Acid, Hydrazine based organic materials and Acetylacetonce are frequently used as a fuel. The water, hydrocarbons and alcohols works as solvent for reactions involved in this synthesis [53].

Thus, combustion synthesis is able to produce nanoparticle of various materials both at research purposes as well as at industrial scale [51, 53–57]. Various kind of nanoparticles like titanates [58], ferrites [59], carbonates [60], hydroxide [61] and oxides [62] are grown using this approach. Combustion synthesis is utilized for growing different kind of MgO nanostructures [63, 64] and its derivative [65–67].

Our group utilizes, this method to synthesize MgO nanoparticles using combustion synthesis while taking magnesium nitrate as an oxidizer and citric acid as fuel [68]. This method shows reproducibility [69]. The following equation is expected during synthesis process.

$$Mg\,(NO_3)_{2.4}H_2O + \text{Citric acid} \rightarrow MgO + CO_2 + NO + H_2O$$

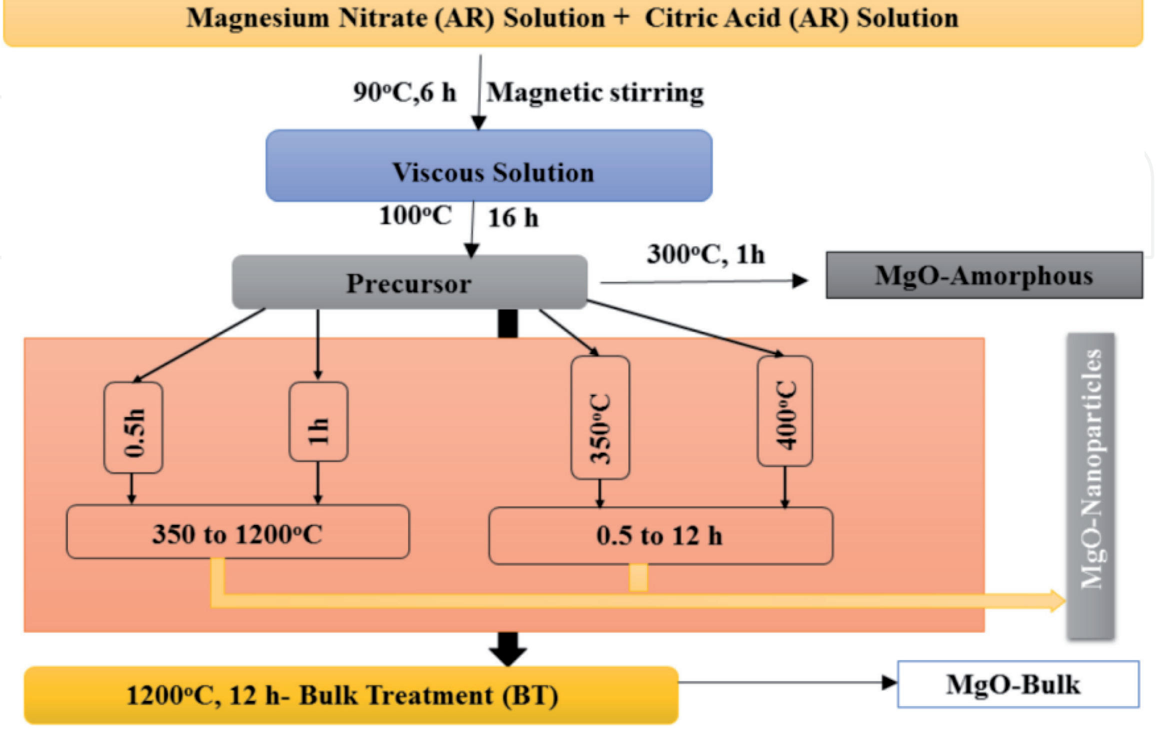

Figure 2.
Synthesis of MgO nanoparticles from magnesium nitrate Ref. [69].

Figure 2 depicts schematic diagram of synthesis process. It is clear that synthesis takes place at low temperature, which reduces cost of synthesis. **Figure 3** shows representative X-ray diffraction (XRD) pattern of the nanoparticle synthesized at 500°C for 1 h. The method is able to produce nanoparticle with pure phase and no other crystalline phases are observed [70].

Green synthesis techniques utilize natural extracts [71] as fuels/oxidizer. Some of the natural extracts for synthesizing MgO nanoparticles are Neem leaves [72], *Artemisia abrotanum* Herba Extract [73], orange fruit [74], Aqueous Eucalyptus globules leaf [75] and Medicinal Plant *Pisonia grandis* R.Br. Leaf [76].

Microwave synthesis utilizes microwave radiation rather than furnace heating in order to avoid longer duration of heating to precursor [77, 78]. This method was successfully applied to form MgO nanoparticles by number of researchers [79–81].

Other methods which are effectively used to grow nanoparticles are facile [82, 83] and miroemulsion synthesis [84–86].

2.2 MgO thin films

Spin coating method is well known tool for growing thin films which utilizes chemical reaction to form materials on the given substrate [87, 88]. Sol-gel chemistry is helpful to synthesize thin films of MgO of desired crystallographic orientation using spin coater [89, 90]. **Figure 4** shows schematic of sol-gel method utilizing a spin coater to grow thin film [91, 92].

Atomic layer deposition (ALD) method allows depositions with excellent uniformity and conformality, with a cost-effective methodology [93, 94]. Thickness and composition control are usually possible over large-area substrates. Thin films of MgO were deposited by atomic layer epitaxy (ALE) from bis(cyclopentadienyl) magnesium and water using soda lime glass and Si(100) as substrates [95]. In another study, MgO films have been grown by atomic layer deposition in the wide

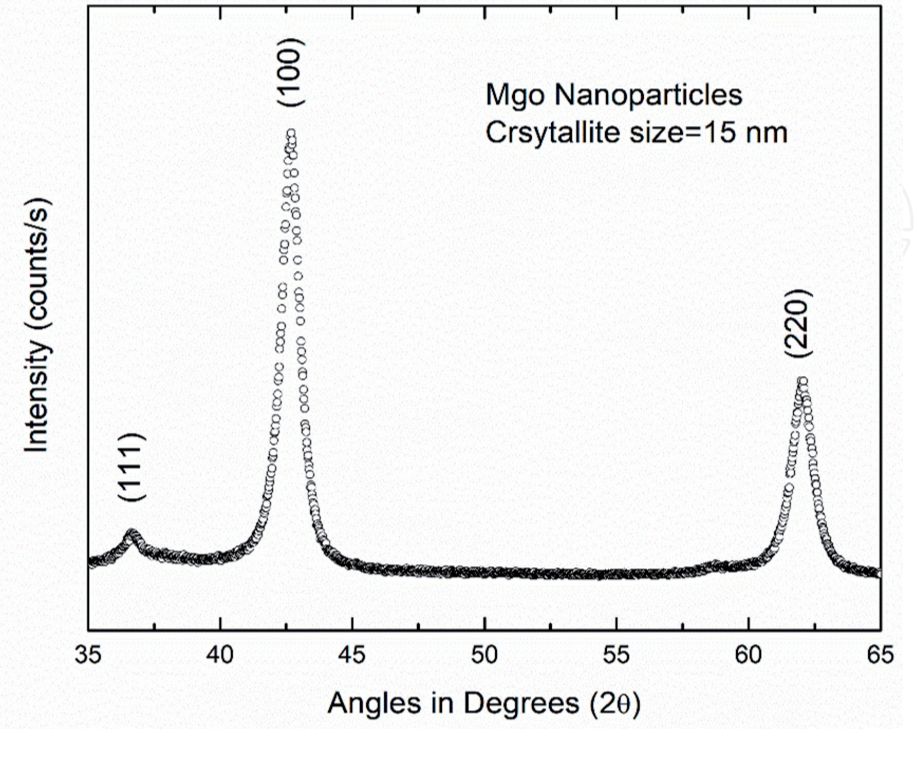

Figure 3.
X-ray diffraction pattern of the nanoparticle synthesized at 500°C for 1 h.

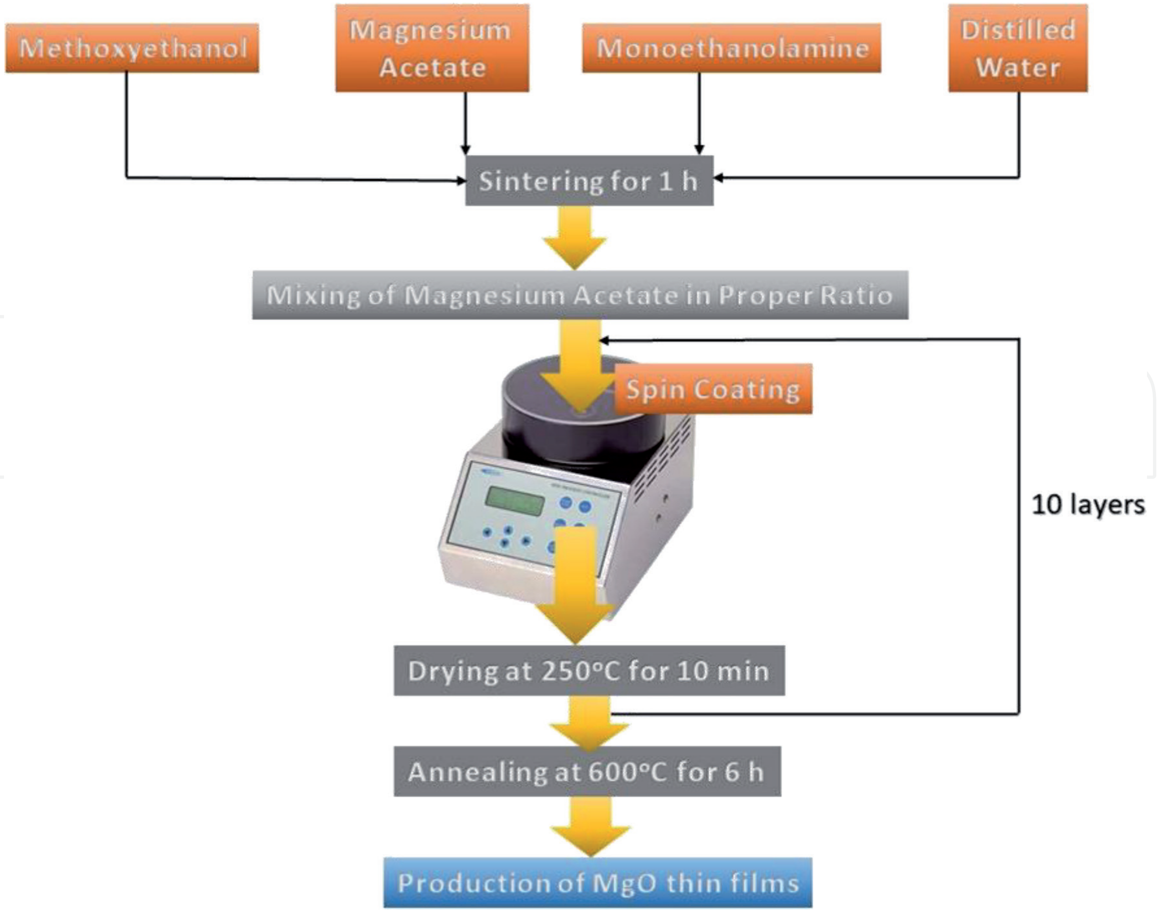

Figure 4.
Schematic of sol-gel spin coating method to grow MgO thin films. This schematic is based on the method described Ref. [91].

deposition temperature window of 80–350°C by using bis(cyclopentadienyl) magnesium and H_2O precursors [96].

3. Top-down approaches

Top-down approaches are mostly utilized to grow thin films of inorganic materials. Some of these methods are discussed here.

3.1 MgO nanoparticle

Mechanical milling/high energy ball milling is well known method which utilizes bulk counterpart as starting material and used for growing nanoparticles of different kind of materials [97, 98]. Depending upon milling process, the milling machines are categories as follows: tumbler ball mills, vibratory mills, planetary mills, and attritor mills [99, 100]. In the ball milling process, powder mixture or bulk powder placed in the ball mill is subjected to high-energy collision from the balls for nanoparticle synthesis. **Figure 5** depicts the schematic of high energy ball milling system [101]. Though this technique is effective to synthesize oxide nanoparticles [102, 103], however, no report is available for synthesizing MgO.

3.2 MgO thin films

Top-down approaches for growing MgO thin films are depicted in this section.

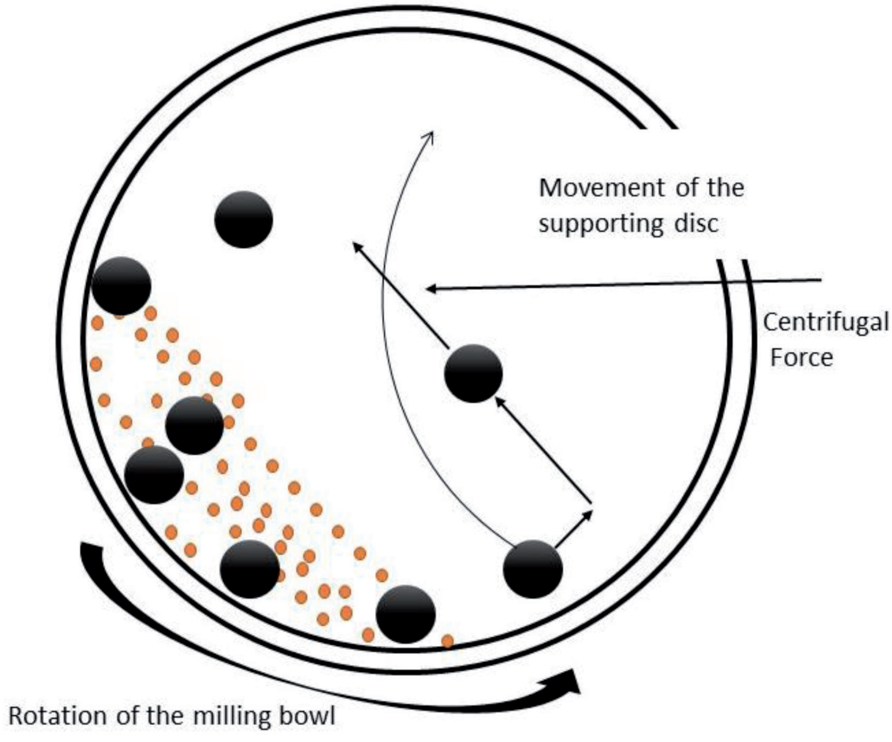

Figure 5.
Schematic of ball-milling process. Redrawn from Ref. [101].

e-Beam evaporation method involves the evaporation of material target with e-beam energy [104]. Schematic of this method is shown in **Figure 6**. This method is effectively used to grow MgO thin films on different type of substrates like NaCl [105], Si [106], fused quartz [107] as well as on metallic layers [108, 109].

Figure 7 shows the MgO thin films on fused quartz substrate along with MgO powder. Both the films of thickness around 5 and 50 nm reveal almost amorphous

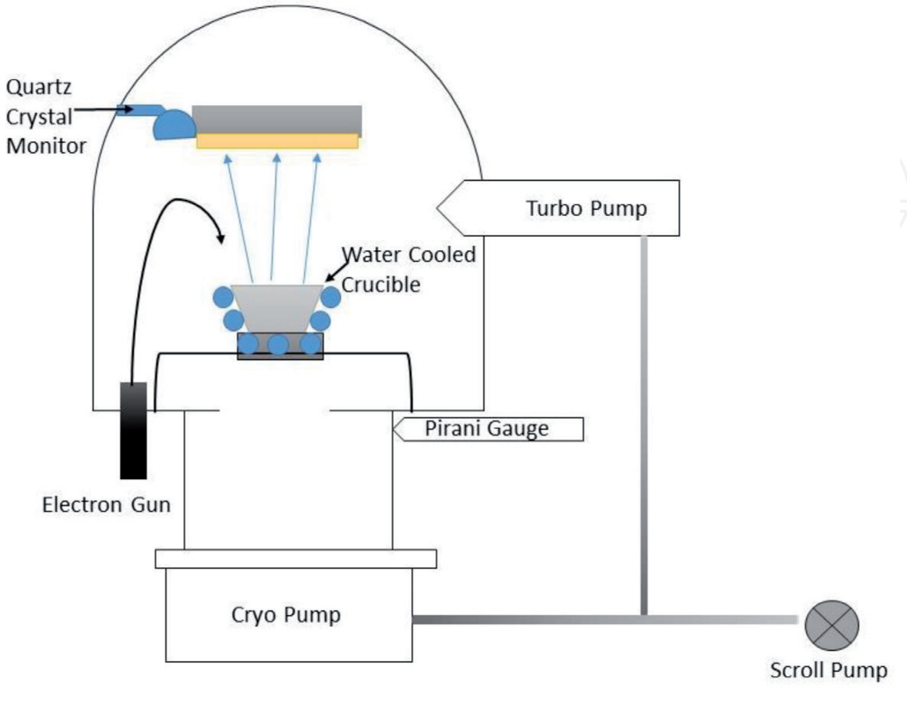

Figure 6.
e-Beam evaporation for growing MgO thin films. Schematic is based on the set-up used for growing MgO thin films in Ref. [107].

nature. Optical absorption spectra of MgO thin films exhibit onset of film formation (**Figure 8**). This method is also utilized to grow MgO thin films on Si substrate. Films grown on this substrate exhibits polycrystalline nature [110].

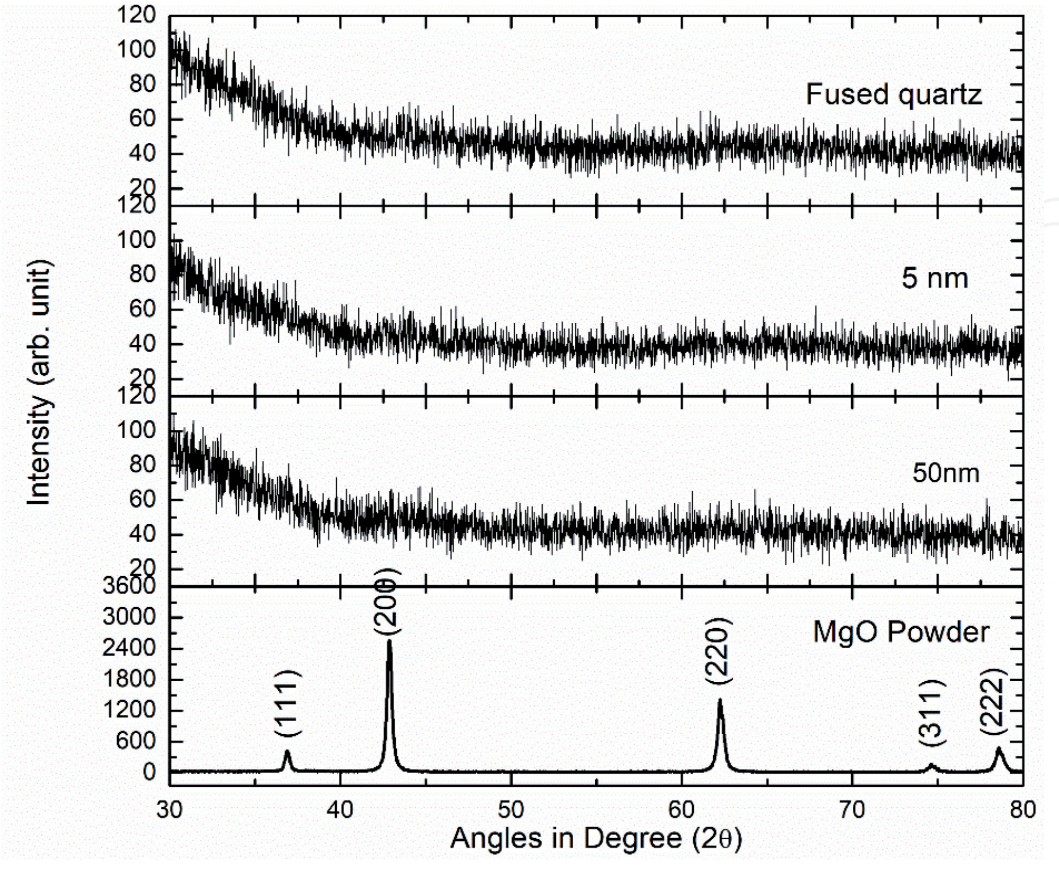

Figure 7.
X-ray diffraction pattern of MgO thin film grown on fused quartz using e-beam evaporation method.

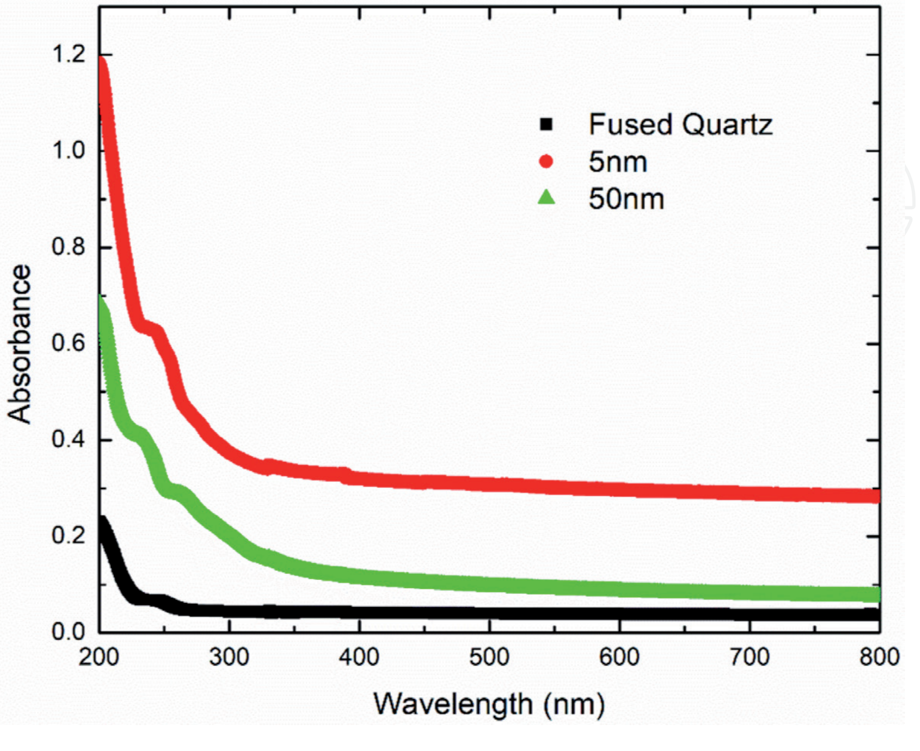

Figure 8.
UV-Vis spectra of MgO thin film grown on fused quartz using e-beam evaporation method.

Molecular beam epitaxy (MBE) utilizes e-beam for growing thin films [111]. It provides better control over stoichiometry ratio but also helpful in epitaxial growth of MgO [112, 113].

Pulsed laser deposition (PLD) as a thin film growth technique was not much popular until the late 1980s, when it has been used to grow superconducting $YBa_2Cu_3O_7$-δ films [114]. Since then, the amount of research involving this technique has increased significantly and a number of compositions have been stabilized in thin film successfully [115–122]. The schematic of PLD system is shown in **Figure 9**. In PLD, a pulsed laser beam (having wavelengths in UV range) strikes the surface of the target material to be deposited. For a short duration of laser pulse (~20 nanoseconds), enormous power (~10 MW) is delivered to the target material and absorption of energy leads to ablation before the thermodynamic equilibrium. The energy from

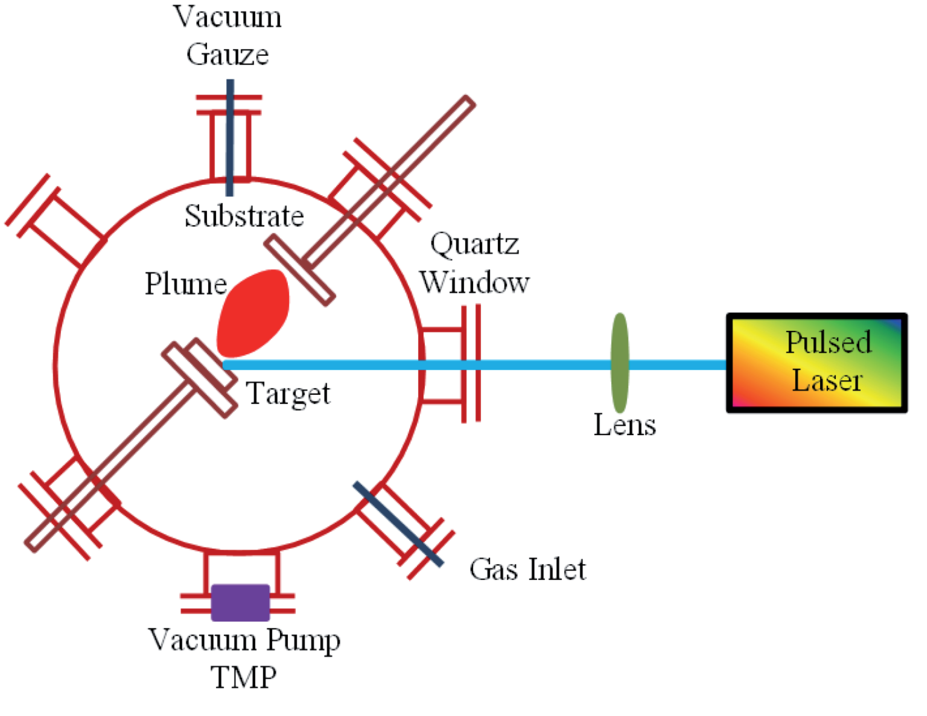

Figure 9.
Schematic of pulsed laser deposition setup.

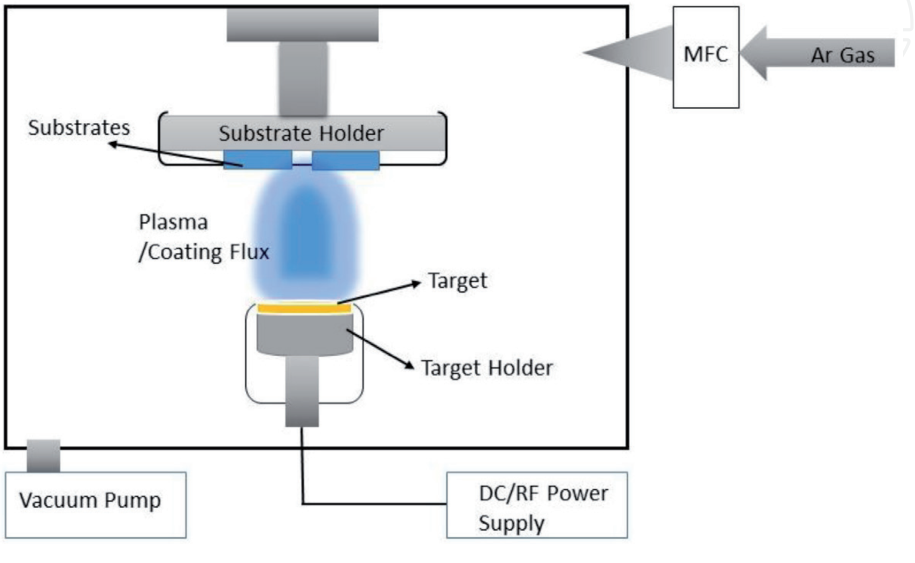

Figure 10.
Schematic of radio frequency sputtering setup based on the work reported in Ref. [131].

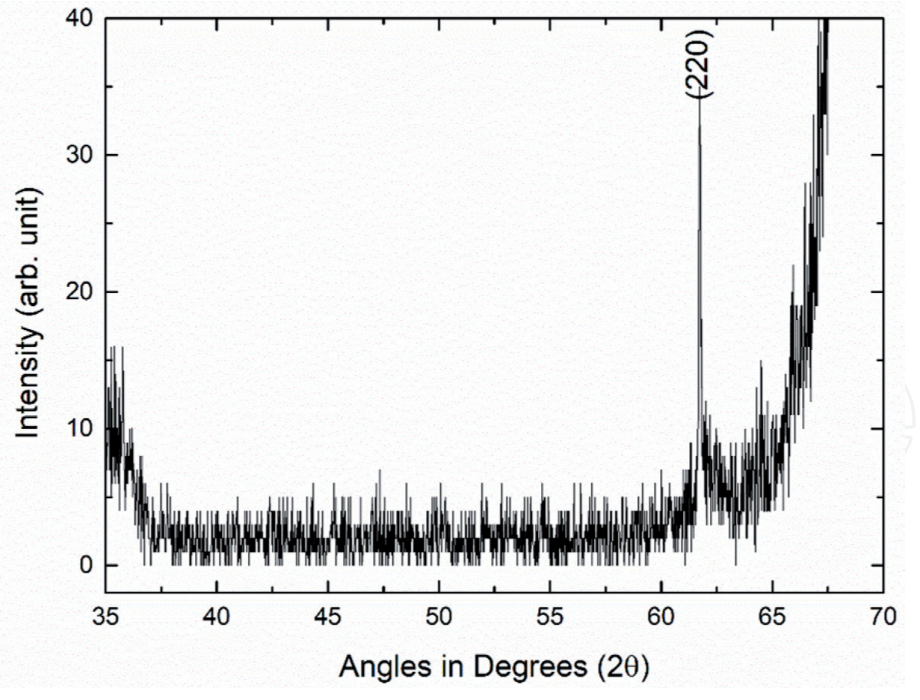

Figure 11.
XRD pattern of MgO thin film grown using rf sputtering method.

the laser evaporates the target's surface and the ablated material forms the plasma plume which finally deposit on the substrate mounted in front of the target.

The main advantage of PLD is the stoichiometric transfer from the multicomponent target to the thin film form, which otherwise is hard to achieve with any other thin film growth technique such as thermal evaporation or sputtering. The pulsed nature of PLD allows precise control on the film growth rates. Some drawbacks of the PLD technique are small area deposition, growth of macroscopic particles (particulates) during the ablation process, defects produced during growth, etc.

These advantages of this method allow researchers to grow MgO films on yttrium stabilized zirconia (111) substrates [123], Si (100) [124] and Al_2O_3 (0001) substrates [125].

Radio frequency sputtering method: At present most desired application of MgO is its utilization as a barrier for magnetic tunnel junction and rf sputtering method is preferred choice [126, 127] as well as for other applications [128]. **Figure 10** shows the rf sputtering setup for the fabrication of thin films.

MgO films on Si substrate are grown by number of researchers [129, 130] as well as by our group [42, 131]. Films grown on Si substrate are both amorphous [132, 133] and crystalline [134, 135] in nature depending upon the deposition time and annealing temperature. **Figure 11** shows the XRD pattern of the MgO thin film grown at substrate temperature of 350°C, deposition time of 400 min and annealing temperature of 800°C for 1 h followed by 300°C and 24 h.

Apart from this, number of groups utilizes **chemical deposition (CVD) method** to grow MgO thin films on different substrates [136–138].

4. Conclusions

Thus, an overview of bottom-up and top-down approaches for synthesis of MgO nanoparticles and thin films is depicted in this chapter. Chemical methods are effective to grow nanoparticles, however, later is successful to grow thin films.

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Conflict of interest

The authors declare no conflict of interest.

Notes/thanks/other declarations

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