STM JOURNALS

International Journal of
Electro-Mechanics and
Material Behavior

Volume 1, Issue 2, 2023
July—December
DOI (Journal): 10.37591/IJEMB

https://journals.stmjournals.com/ijemb

Review IJEMB

The Impact of Distinct Dopant Elements (Cu and Al) on the Electrochemical Characteristics of MgO Thin Films Formed Using the Electrodeposition Technique

Mahadev T. Mhetre[1], Balkrishna J. Lokhande[2,*]

Abstract

By using an aqueous electrodeposition technique, copper (Cu) and aluminum (Al) doped magnesium oxide (MgO) thin films were created. We examined how the dopant elements affected the electrochemical characteristics of MgO thin films deposited on stainless steel (SS) substrates in the current study. We annealed the MgO-based films at 450◦C. The MgO films doped with Cu and Al have been determined by X-ray diffraction (XRD) results. Cyclic voltammetric analyses (CV), galvanostatic charge-discharge (GCD) technique, are the electrochemical methods. The redox behavior of both Cu and Al-doped and pristine MgO during the CV is confirmed by peaks in the CV curves. There was a maximum of 24.16 Fg-1 in the measured specific capacitance (SC) of Al-doped MgO. In contrast to typical capacitors, GCD analysis reveals distinct behavior. The charging and discharging times were found nearly the same for different applied currents.

Keywords: Electrodeposition technique, elements, Cyclic voltammetric analyses, medical devices, EDLC

INTRODUCTION

The wearable and portable electronics that have revolutionized our way of life are an indispensable part of the modern world. Our lives have been made more convenient by, among other things, multifunctional cell phones, healthcare, activity trackers (smartwatches and sensors), and implantable medical devices (pacemakers, insulin pumps, and many more). However, efficient energy storage systems are required due to the rising energy consumption of these smart electronic devices. Notably, the development of portable electronic appliances is made possible by the extended cycle and calendar life, high power and rate capability, and safe operations of supercapacitors (SCs), one of the various electrochemical energy storage (EES) technologies. Comparing conventional electric double-layer capacitors (EDLC) to other devices like batteries, EDLCs provide superior power delivery since they store charges electrostatically at the electrode/electrolyte interface (a non-Faradaic process). However, the SCs' low energy storage capacity (5–10 Wh/kg) and high power density (~15 kW/kg) are commonly achieved with modern carbonaceous materials, which limits the applications for which they can be used. Aside from the high-power supply, there is a huge demand for high energy in a number of recent and prospective applications, such as electric vehicles and renewable energy storage.

***Author for Correspondence**
Balkrishna J. Lokhande
E-mail: bjlokhande@yahoo.com

[1]Student, Santosh Bhimrao Patil Arts, Commerce, and Science College, Mandrup, South Solapur, Solapur, Maharashtra, India
[2]Professor, Lab of Electrochemical Studies, School of Physical Sciences, Punyashlok Ahilyadevi Holkar Solapur University, Solapur, Maharashtra, India

Received Date: January 25, 2024
Accepted Date: February 05, 2024
Published Date: March 28, 2024

Citation: Mahadev T. Mhetre, Balkrishna J. Lokhande. The Impact of Distinct Dopant Elements (Cu and Al) on the Electrochemical Characteristics of MgO Thin Films Formed Using the Electrodeposition Technique. International Journal of Electro-Mechanics and Material Behavior. 2023; 1(2): 12–17p.

Pseudocapacitive materials have arisen in the search for high energy and high power devices at the same time. They feature completely different electrochemical properties and a current response that is neither simple capacitive nor bulk Faradaic (like batteries). These materials, however, conduct fast and reversible surface-controlled redox reactions at the electrode surface by either intercalating or adsorbing electrolyte ions; hence, they offer a way to produce high energy and high power densities. Although the extremely high rate capabilities of pseudocapacitive materials are similar to those of double-layer capacitive materials (EDLC), they are not the same as EDLC because their charge storage is based on redox reactions similar to those in batteries. Furthermore, the redox reaction kinetics are incredibly quick and unrestricted by semi-infinite diffusion, setting them apart from conventional battery materials. Stated differently, although they are not electrostatic in nature, pseudocapacitors can be viewed as an auxiliary type of EDLC. Their charge/discharge patterns and cyclic voltammetry electrochemical fingerprints are comparable to those of EDLC. The background information and Conway's rationale for designating such things as "pseudocapacitance" have been eloquently provided by Brousse and colleagues. Therefore, in order to distinguish them from EDLC in terms of the charge storage mechanism and to describe the features of an electrode that displays the electrochemical signature of a capacitor (CV and GCDs), the prefix "pseudo" combined with "capacitor" is utilized.

Magnesium oxide thin films have significant application features that are generating a lot of interest in science and technology [1]. MgO thin films are used extensively in solar cells, photodetectors, light-emitting diodes, optoelectronic devices, and sensors [1-3]. MgO exhibits exceptional broad band gap characteristics as well as chemical and thermal stability [1, 2]. Doping, in general, is a helpful method that dramatically alters the characteristics of host materials. Doping with a transition-metal cation opens up energy levels between the valence and conduction bands and d-d transitions, which closes the band gap [4]. A variety of dopants, including Ag, Zn, Fe, and Cr, have been employed to alter the characteristics of MgO thin films [5-8]. We have selected Al and Cu as the doping elements in this work since they are inexpensive, easily obtainable, and non-toxic materials. Additionally, Cu, a divalent metal cation, replaces Mg with extra electrons, giving Al, a trivalent cation, additional electrons that may enhance the opto-electrical capabilities. The only research on Al-doped MgO thin films that we are aware of is as follows [9]. To examine the nano-mechanical and optical properties, Payel Maiti et al. [7] spin-coated their Al-doped MgO films onto a quartz substrate. They [9] said that the refractive index value, transmittance, and elastic modulus of their deposited film are all noticeably greater.

This paper reports on the electrodeposition method's production of MgO (0.2 M) thin films doped with Cu and Al at 2% concentrations. With the use of X-ray diffraction (XRD), the physical characteristics of the produced MgO films containing Cu and Al dopant elements were reviewed. We also obtained the electrochemical results of MgO films doped with Cu and Al in addition to these analyses. Present and discussed in the appropriate sections were the results collected for the grown Cu and Al-doped MgO films.

EXPERIMENTAL

Materials

Mg(NO3)2.6H2O was obtained from SD Fine Chemicals and utilized as a source of Mg in the synthesis activity. Strips of 304-grade stainless steel (SS) measuring 1 cm X 5 cm were employed as conducting substrates. During the experiment, the solvent was deionized (DI) water.

Electrode Preparation

The doped Magnesium oxide (MgO) thin films were prepared by electrodeposition method using a laboratory system. For sample preparation, an SS substrate of 1cm × 5cm was cut. The further substrate was polished roughly with zero-number polish paper and ultrasonically cleaned for 15 minutes. After that, the 60 ml of precursor, of aqueous solution of 0.2 M Magnesium nitrate Mg(NO3)2.6H2O obtained by dissolving in DI water under constant stirring was used. For doping elements like Aluminum nitrate [$Al(NO_3)_3$] and cupric nitrate [$Cu(NO_3)_2$] of 20 ml each with 0.2 molarity were prepared by dissolution

in DI water under constant stirring. Further by using the electrodeposition method 20 ml was doped with 2% of the above-mentioned compounds for 20 minutes at 20 mA applied current. MgO thin film doped with Cu & Al was obtained after annealing at 450°C. Finally, the electrochemical characterisation of all the samples was studied. Among these electrodes, the Al-doped MgO electrode exhibits an excellent value of specific capacitance.

Characterization of Thin Films

By weighing the substrate both before and after the deposition, the weight difference approach was used to calculate the weight of the active ingredient that was deposited. The structural characteristics of the generated materials were investigated using X-ray diffraction (XRD) (Bruker AXS Analytical Instruments Pvt. Ltd., Germany, Model: D2 phaser). A CHI machine was used in a three-electrode setup to carry out the electrochemical tests of the thin films, including stability, galvanostatic charge-discharge (GCD), cyclic voltammogram (CV), and electrochemical impedance spectroscopy (EIS).

RESULTS AND DISCUSSIONS

XRD analysis was used to look at the phase and crystal structure [10]. The successful synthesis of MgO was confirmed by the XRD pattern, which showed peaks at 42.9° (200) and 62.24° (220). The phase structure of MgCuO was confirmed by the peak positions at 42.90° (200) and 62.24° (220), which corresponded to Cu-doped MgO and was consistent with the JCPDS card 77–2183. High crystallinity was indicated by sharp, narrow peaks (Figure 1). The Al-doped MgO's XRD pattern was obtained. It showed peaks at 42.90° (200), 44.80° (400), and 62.38° (220), all of which were in agreement with the JCPDS card 77–034 and had a $MgAl_2O_4$ phase structure. The diffractogram of the as-synthesised sample showed an extra peak of SS substrates and a higher intensity peak at $2\theta = 42.90$, indicating that Cu-doped MgO and Al-doped MgO had been successfully fabricated. Furthermore, Cu's ionic radius (0.073 nm) was found to be relatively larger than Mg's (0.072 nm), and Al's ionic radius (0.067 nm) is also greater. As a result, Al and Cu can be doped in the MgO crystal lattice with ease. By Eq. (1), the grain size was estimated.

$$D = \frac{0.9\lambda}{\beta \cos \theta} \tag{1}$$

where the grain size, wavelength, full width at half maximum, and Bragg's angle are represented, respectively, by D, λ, β, and θ. According to the data, the average particle sizes of MgO doped with Al and MgO doped with Cu are 16.16 nm and 21.49 nm, respectively.

In 1M KOH, the constructed sample electrode was scanned at various scan rates ranging from 5 mV/s to 100 mV using cyclic voltammetry (CV) analysis (Figure 2a and 2b). The sample's pseudocapacitive behavior is shown by the obtained curves. Due to the electrodes' reversible nature, the CV curves exhibit maxima at the corresponding anodic and cathodic sweeps. The current integral and, thus, the area under the curve were found to increase as the scan rate increased. It is also noticed that as the scan rate increases the value of specific capacitance (SC) decreases, this is due to low reaction time. Table 1 shows Al-doped MgO gives a 24.16 F/g, and Cu-doped MgO gives a 16.37 F/g. Comparing these two Al-doped MgO gives excellent SC. The following formula is used to calculate the SC of the prepared electrode from the CV curves.

$$SC = \frac{C}{m} = \frac{\int_{V_1}^{V_2} Idv}{m(V)\frac{dV}{dt}}$$

where dv/dt is the potential scan rate, C is the capacitance, m is the weight of the active material submerged in the electrolyte, V = V2-V1 is the potential window, and I is the average current in the Redox cycle.

Additionally, the electrochemical performances of the annealed Al-doped and Cu-doped MgO thin films were investigated using galvanostatic charge-discharge (GCD) cycles, as illustrated in Figures 2c.

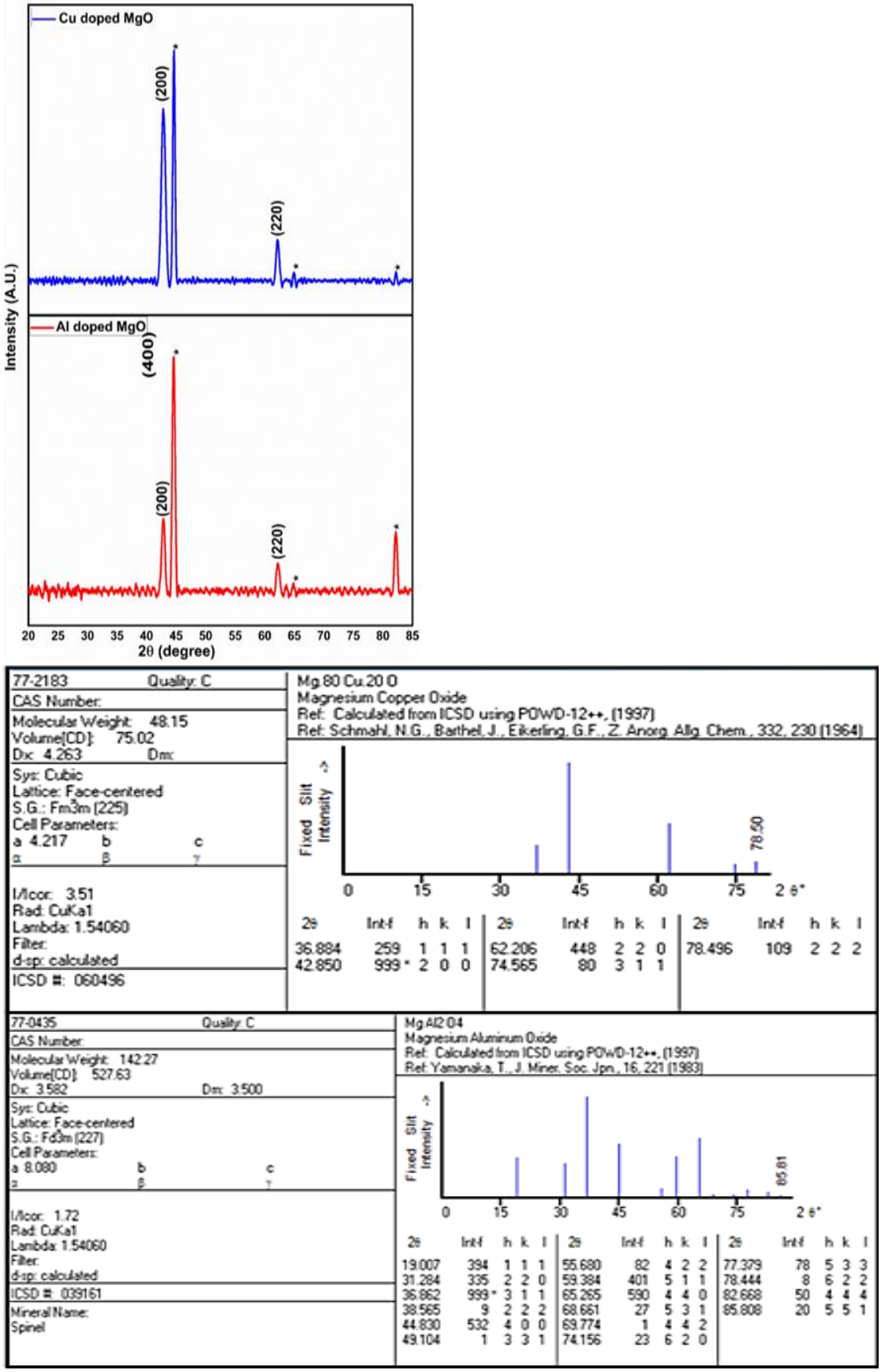

Figure 1. XRD Pattern of Cu-doped MgO and Al-doped MgO.

Table 1. Specific capacitance by CV curve.

Scan Rate	Specific Capacitance (SC) F/g	
	Al-doped MgO	***Cu-doped MgO***
5	24.16	16.37
10	18.93	15.60
20	14.16	13.77
50	10.74	11.56
100	8.61	9.67

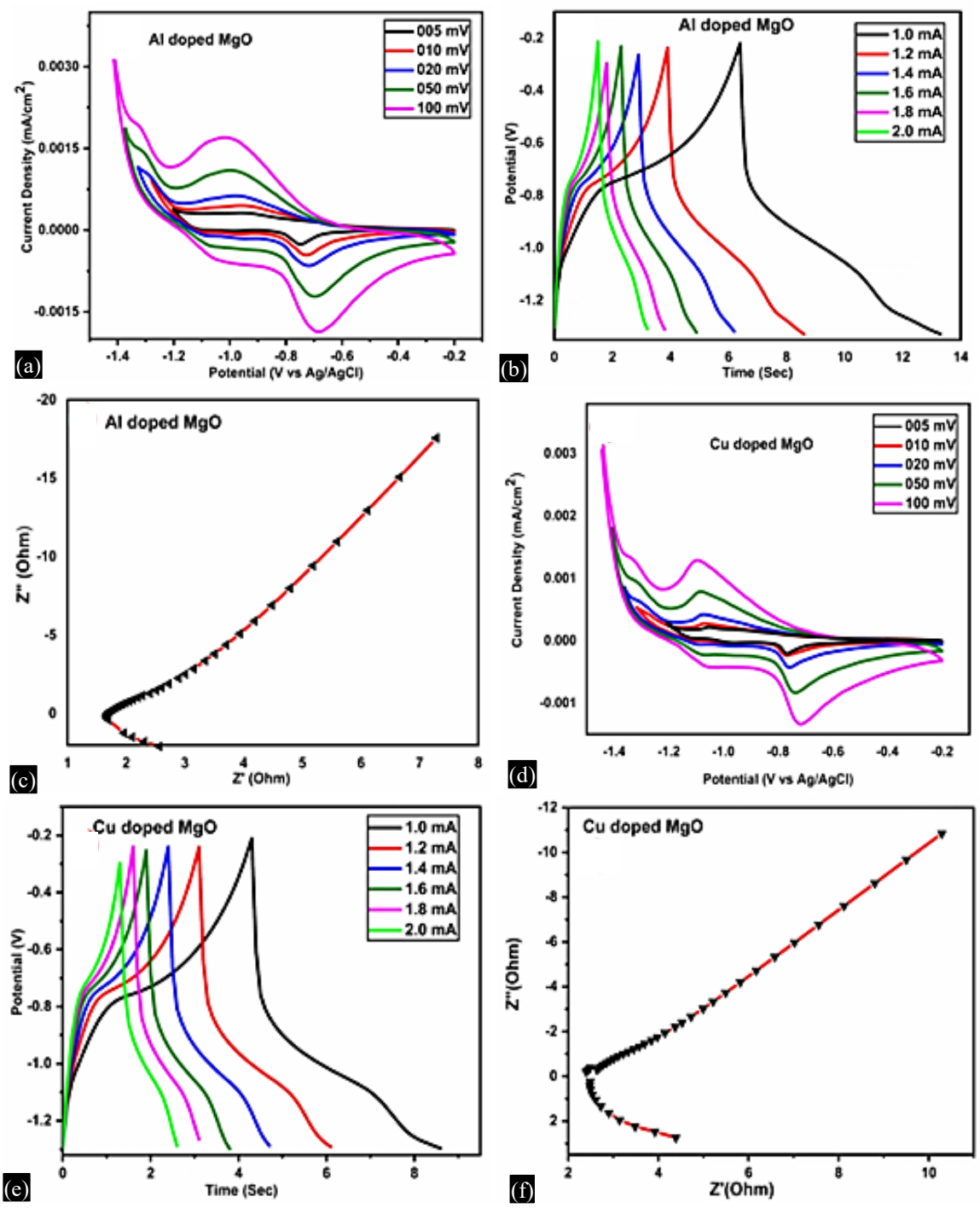

Figure 2. CV, GCD and EIS curve of Al-doped MgO and Cu-doped MgO.

The GCD study was conducted at 0.001-0.002 Acm-2 current density between -1.2 to -0.2 V potential window in 1 M aq. KOH. The pseudocapacitive character of the Al-doped and Cu-doped MgO is confirmed by the results, which show that all of the curves are symmetric and linear with regard to time. The completely linear charging and discharging portions of the curves show that K+ is surface-intercalated inside the Al- and Cu-doped MgO matrix. The small equivalent series resistance (ESR) of the Cu- and Al-doped MgO is the cause of the sudden drop in potential at the start of the discharge cycles.

The annealed Al-doped and Cu-doped MgO thin film electrodes' electrochemical impedance spectra (EIS) were also measured, and the results are displayed in Figures 2c and 2f. The EIS ranges from 1 MHz to 100 Hz at an amplitude of 5 mV. In the low-frequency zone, both thin-film samples exhibit a straight line; in the high-to-medium frequency region, they display a depressed semicircle; and in the real Z' axis, they exhibit a high-frequency intercept. The samples show the overall ohmic resistance (Rs) at the high-frequency intercepts. This is the result of the interaction between the active materials' contact resistance and the current collector, as well as the electrolyte's ionic resistance and intrinsic resistance.

CONCLUSION

Electrodeposition was successfully used to generate Al-doped MgO and Cu-doped MgO thin films. The crystalline nature of thin films is shown by XRD spectra. On the other hand, it was determined that the average crystallite size of the Cu- and Al-doped MgO thin films was 21.49 nm and 16.16 nm, respectively. The CV curve electrochemical investigations revealed that the maximum SC is obtained from Al-doped MgO.

REFERENCES

1. Carta G, El Habra N, Crociani L, Rossetto G, Zanella P, Zanella A, Paolucci G, Barreca D, Tondello E. CVD of MgO thin films from bis (methylcyclopentadienyl) magnesium. Chemical vapor deposition. 2007 Apr;13(4):185-9.
2. Moses Ezhil Raj A, Nehru LC, Jayachandran M, Sanjeeviraja C. Spray pyrolysis deposition and characterization of highly (100) oriented magnesium oxide thin films. Crystal Research and Technology: Journal of Experimental and Industrial Crystallography. 2007 Sep;42(9):867-75.
3. M. T. Mhetre, H. M. Pathan, A. V. Thakur and B. J. Lokhande, Preparation of Magnesium Oxide (MgO) Thin Films by Spray Pyrolysis and Its Capacitive Characterizations. ES Energy Environ., 2022, 18, 41-46 ES
4. Nion, M. Golam Mortuza, et al. "Effect of Al doping on morphology and optical properties of spray pyrolized MgO thin films." *Results in Materials* 12 (2021): 100235.
5. Yu HK. Secondary electron emission properties of Zn-doped MgO thin films grown via electron-beam evaporation. Thin Solid Films. 2018 May 1;653:57-61.
6. Benedetti S, Nilius N, Valeri S. Chromium-doped MgO thin films: morphology, electronic structure, and segregation effects. The Journal of Physical Chemistry C. 2015 Nov 12; 119(45): 25469-75.
7. Maiti P, Das PS, Bhattacharya M, Mukherjee S, Saha B, Mullick AK, Mukhopadhyay AK. Transparent Al+ 3 doped MgO thin films for functional applications. Materials Research Express. 2017 Aug 14;4(8):086405.
8. Islam MR, Rahman M, Farhad SF, Podder J. Structural, optical and photocatalysis properties of sol–gel deposited Al-doped ZnO thin films. Surfaces and Interfaces. 2019 Sep 1;16:120-6.
9. Awwad A, Salem N, Amer M, Shammout M. Adsorptive removal of Pb (II) and Cd (II) ions from aqueous solution onto modified Hiswa iron-kaolin clay: Equilibrium and thermodynamic aspects. AM Awwad, NM Salem, MW Amer and MW Shammout. Adsorptive removal of Pb (II) and Cd (II) ions from aqueous solution onto modified Hiswa iron-kaolin clay: Equilibrium and thermodynamic aspects. Chemistry International. 2021 Jun 13;7(2):139-44.
10. Shammout M, Awwad A. A novel route for the synthesis of copper oxide nanoparticles using Bougainvillea plant flowers extract and antifungal activity evaluation. MW Shammout and AM Awwad. A novel route for the synthesis of copper oxide nanoparticles using Bougainvillea plant flowers extract and antifungal activity evaluation. Chemistry International. 2021 Jun 13;7(1):71-8.

