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Effects of Al and Mn Dopant on Structural and Optical Properties of ZnO Thin Film Prepared by Sol-Gel Route

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ABSTRACT

Undoped, 10 wt% Al and 10 wt% Mn doped ZnO thin films were deposited on a glass substrate by sol-gel dip coating. Al ions played an important role in improvement of the c-axis orientation, while Mn ions inhibited the growth along c-axis. The average grain size decreased when doping ZnO with Al and Mn. The smallest average grain size was 25 nm, obtained with 10 wt% Mn doping. The band gap values of prepared thin films varied in the range of 3.24 - 3.96 eV.

Keywords: ZnO, thin film, doping effect, structural properties, optical properties

INTRODUCTION

For a decade, there has been a great growing interest in nanomaterials including nanocrystalline powders and thin films because of its distinguishable difference in properties from macroscopic and bulk materials. Research in this area has focused on the synthesis, characterizations and applications of nanometer-sized metals, semiconductors and ceramics. As far as nanomaterials are concerned, zinc oxide (ZnO) is a promising candidate for many applications due to its unique properties. ZnO is an n-type II-VI semiconductor with wide band gap energy of 3.37 eV and exciton binding energy of about 60 meV at room temperature [1]. ZnO naturally forms a hexagonal wurtzite structure and the lack of center of symmetry combining with a large electrochemical coupling, results in strong piezoelectric and pyroelectric properties. Thus, ZnO nanomaterials have been used in room temperature UV lasers [2], short-wavelength optoelectronic devices [3], piezoelectric sensors [4], photoconductors [5], gas sensors [6] and solar cell applications [7].

ZnO thin films have been prepared by various techniques such as chemical vapor deposition [8], rf magnetron sputtering [9], spray pyrolysis [10], pyrosol [11], chemical bath deposition [12] and sol-gel [13] methods. Among them, the sol-gel method has gained worldwide interest because this method offers several advantages such as its high chemical homogeneity, low processing temperature, the possibility of controlling the size and morphology of particles or grains, simplicity and low cost. These advantages make the sol-gel method the most attractive for further development. Therefore, the aims of this report are to prepare Al and Mn doped ZnO thin films by sol-gel dip coating and investigate the correlation of structural and optical properties of prepared thin films at 10 wt% metal doping level.

MATERIALS AND METHODS

All reagents used in this experiment are analytical grade and used without further purification. In order to deposit Al doped ZnO (AZO) and Mn doped ZnO (MZO) thin films, the precursor solutions were prepared from zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$, Merck), aluminium chloride hexahydrate ($AlCl_3.6H_2O$, Aldrich) and manganese chloride tetrahydrate ($MnCl_2.4H_2O$, Aldrich) which were used as Zn, Al and Mn sources, respectively. In addition, polyvinylpyrrolidone (PVP, M.W. 40,000, Fluka) is used as stabilizer. First, 0.2195 g $Zn(CH_3COO)_2.2H_2O$ was dissolved in 10 mL ethanol at room temperature and 90 μL of distilled water was slowly

dropped into the solution with continuous stirring for 15 min so that a hydrolysis reaction was provoked. Later on, 0.0241 g $AlCl_3.6H_2O$ and 0.0198 g $MnCl_2.4H_2O$ were added into each prepared $Zn(CH_3COO)_2.2H_2O$ solutions such that the Al and Mn doping level was 10 wt%. Finally, 0.4 g PVP was added to each precursor solution and these solutions were continuously stirred for 24 h at room temperature to complete the condensation reaction before using as starting sols in the dip-coating process. In this study, the AZO and MZO thin films were deposited on glass substrates. Before dipping the substrate into the precursor sol, the glass substrates were cleaned in mixed solution of hydrochloric acid (HCl) and nitric acid (HNO_3) with a ratio of 1:2 for 10 min. The substrates were then rinsed with distilled water and ethanol for several times and they were finally dried at room temperature. Each layer of as-deposited films was dried at 80 °C in air for 15 min. The dipping process was repeated 5 times after each layer cooled down to room temperature. Finally, all as-deposited films were calcined at 550 °C in air for 1 h to obtain the undoped ZnO, AZO and MZO thin films.

The structural properties of thin films were examined by X-ray diffractometer (XRD, SEIFERT) in the 2θ range of 30 - 70 degrees using CuK_α (λ = 0.15406 nm) radiation, scanning electron microscopy (SEM, JSM-5800LV, JEOL) and atomic force microscopy (AFM, SPA 400). The optical properties of thin films were measured using UV-Vis spectroscopy (UV-Vis, Shimazu 3100) in the wavelength of 200 - 2000 nm.

RESULTS AND DISCUSSION

Structural properties

The crystal structure of representative thin films was carried out by XRD as shown in **Figure 1**. The XRD patterns of undoped and AZO thin films exhibited a strong orientation towards (002) plane or c-axis, whereas there was no preferred orientation in case of MZO thin films.

There are many explanations about the formation of c-axis orientation; for example, the c-axis orientation occurs due to a minimization of the internal stress and surface energy [2] and c-axis orientation could also result from an easy growth because of the high atomic density along (002) plane [14]. In this study, we found that Al ions improved the c-axis orientation that is to say the substituted Al ions at zinc sites in the wurtzite structure can reduce the surface energy as previously mentioned. In contrast, the substituted Mn ions at zinc sites deteriorated the host structure. Based on the ionic radius: (Zn^{2+} = 0.60 Å, Al^{3+} = 0.54 Å and Mn^{2+} = 0.66 Å), the internal stress of MZO thin films is higher than AZO thin films because of the larger ionic radius of Mn^{2+}, so the

MZO structure is more deformed than that of the AZO thin films. Therefore, Mn ions may act as inhibitors for the growth of ZnO along (002) plane during the deposition process.

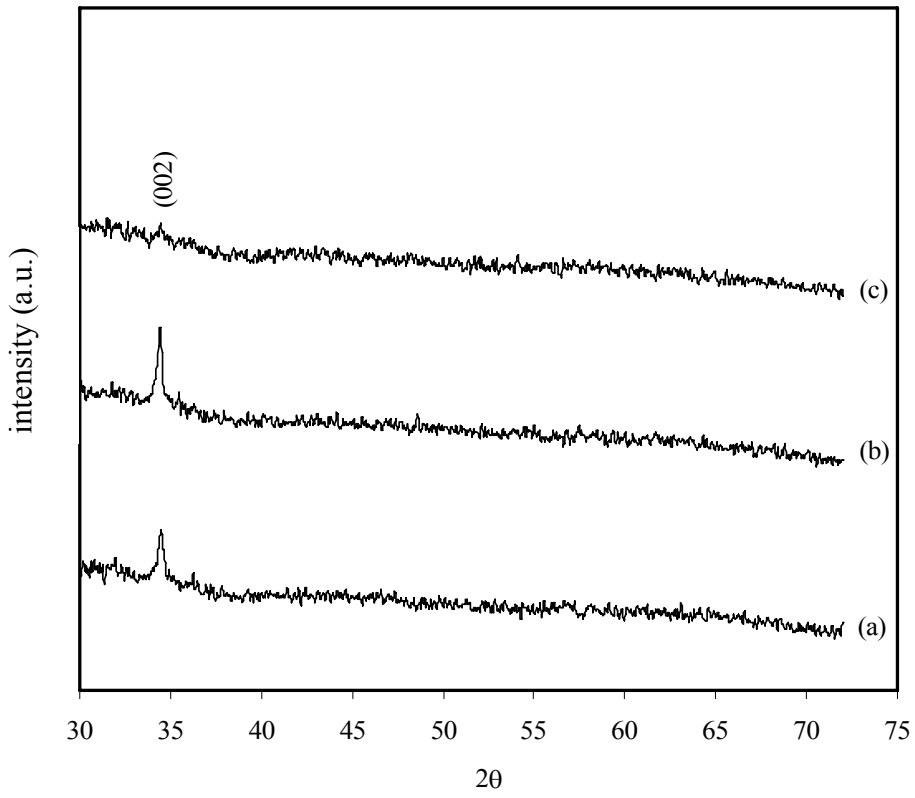
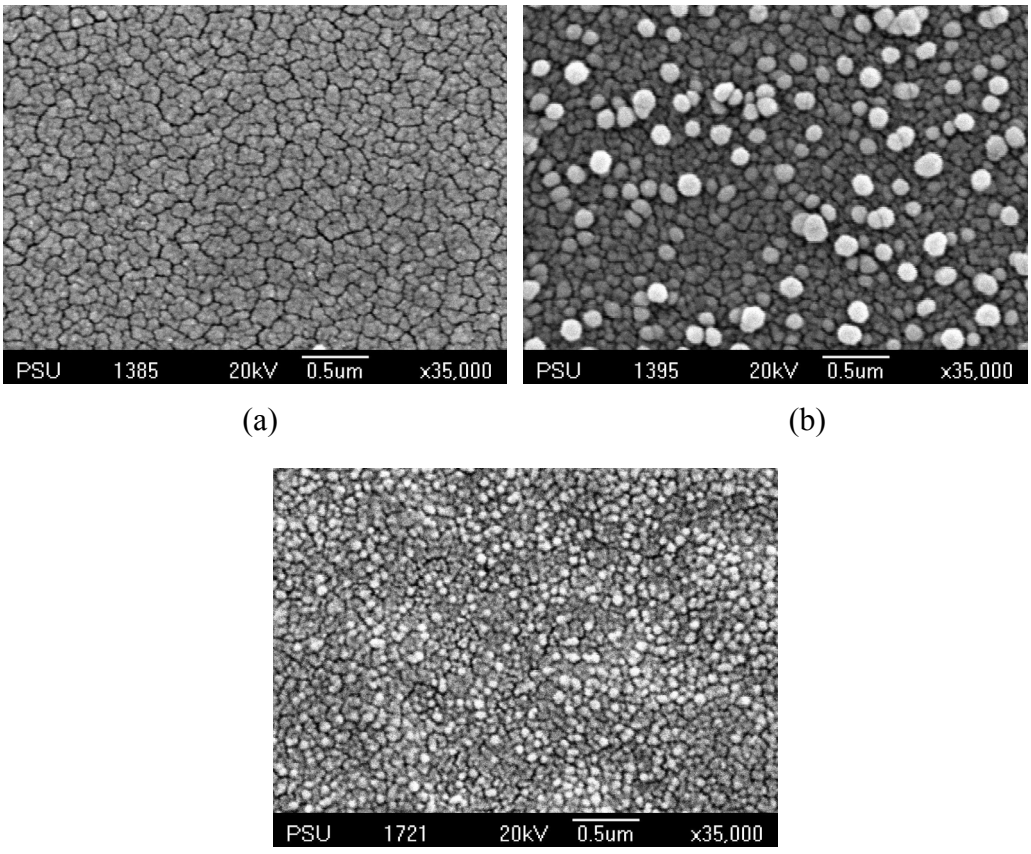


Figure 1 XRD patterns of (a) undoped ZnO, (b) 10 wt% AZO and (c) 10 wt% MZO thin films.

The Al and Mn ions not only affected the c-axis orientation in this study, but also the grain size. **Figure 2** depicts the surface morphological study of undoped, AZO and MZO thin films. It had been observed that the AZO thin film exhibited a predominant rod shape (white hexagonal ZnO particles in **Figure 2b**), as a result of the high degree of c-axis orientation. The SEM images also showed that the average grain size of undoped, AZO and MZO thin films is about 156, 90 and 60 nm, respectively. This average grain size was measured from the difference between visible grain boundaries of cross-sectional images that are not present in this paper. **Figure 3** shows the three dimensional AFM images taken at a scan area of 1.0 × 1.0 μm^2. The

AFM analysis indicates that the average grain size of undoped, AZO and MZO thin films is about 101, 50 and 25 nm, respectively. The average grain size in this case was measured from the difference between visible grain boundaries at the surface. This result is in good agreement with the average grain size from the SEM data. In fact, there is some information indicating that the interstitial zinc plays an important role in controlling grain growth of ZnO thin films. In this case, the concentration of interstitial zinc was decreased because of the Al and Mn dopants. So, the grain growth of ZnO was inhibited because the diffusivity was decreased [15]. It may also be possible that the substituted Al and Mn provided a retarding force within the wurtzite structure opposing the driving force of grain growth and the grain growth was subsequently inhibited [16]. Therefore, in this study it is clear that the Al and Mn play an important role in decreasing the grain size of ZnO.



(a) (b)

(c)

Figure 2 SEM images of (a) undoped ZnO, (b) 10 wt% AZO and (c) 10 wt% MZO thin films.

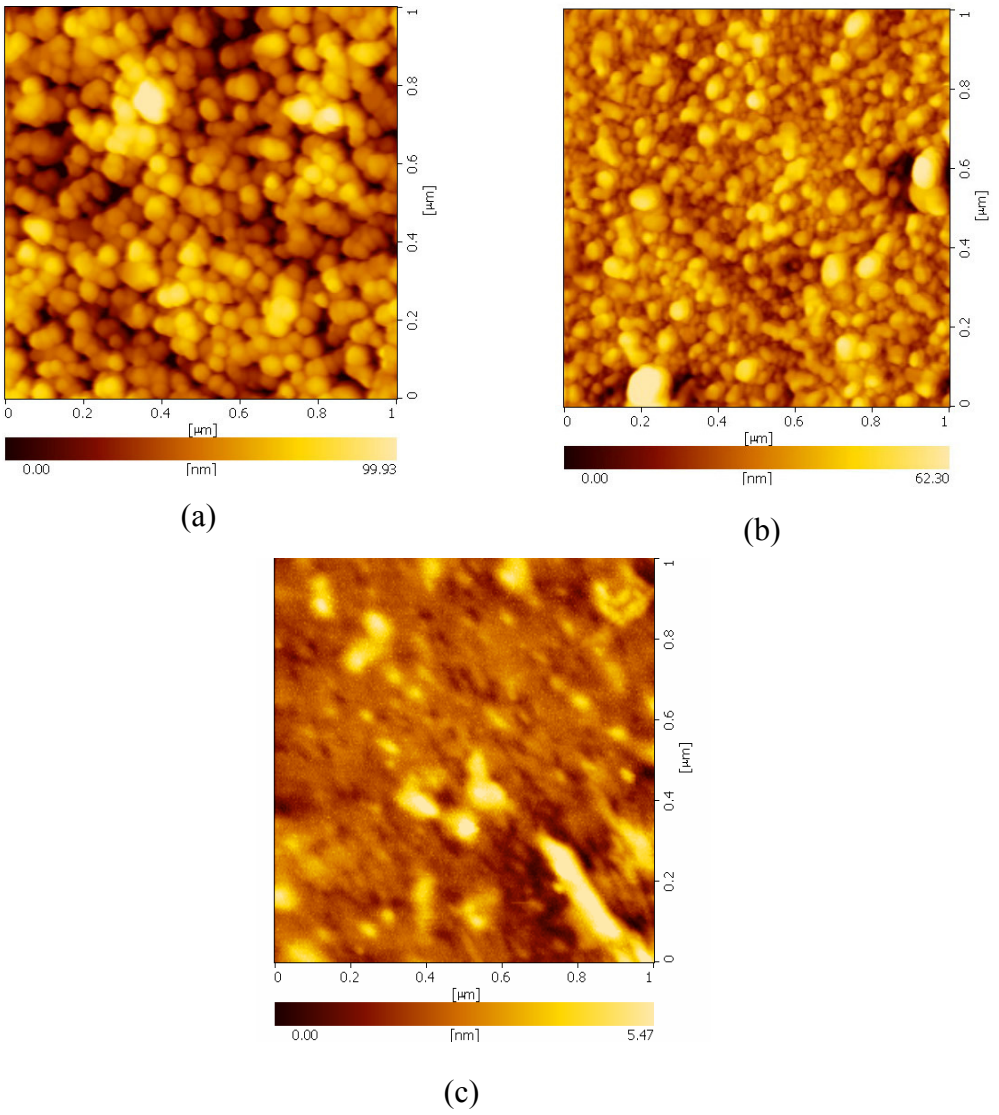


Figure 3 AFM images of (a) undoped ZnO, (b) 10 wt% AZO and (c) 10 wt% MZO thin films.

Optical properties

The high transmission in the visible region is a very important factor in many applications. So, the transmittance of all representative thin films was studied by UV-Vis spectroscopy at room temperature. **Figure 4** shows the transmittance spectra of deposited thin films. The results show that the transmittance is higher than 80 % in all thin films. The theory of optical

transmission gives the relationship between the absorption coefficient (α) and photon energy ($h\nu$) for direct transition as $(\alpha h\nu)^2 = (h\nu - E_g)$ where E_g is the band gap. This band gap can be estimated by extrapolation of the linear portion of an $(\alpha h\nu)^2$ vs $(h\nu)$ plot as given in **Figure 5**. The value of the band gap is enhanced from 3.24 eV (undoped ZnO thin film) to 3.96 and 3.80 eV in the case of doping with 10 wt% Al and 10 wt% Mn, respectively. The increase in the band gap or blue shift can be explained by the Burstein-Moss effect [17]. That is the Fermi level lifts into the conduction band. Consequently, the filling occurs in the conduction band and the absorption transitions occur between the valence band and Fermi level in the conduction band instead of the valence band and the bottom of the conduction band as usual. In this case, the blue shift of absorption edges and the development of states within the gap were also evident when the Al and Mn ions were substituted into the ZnO lattice [18].

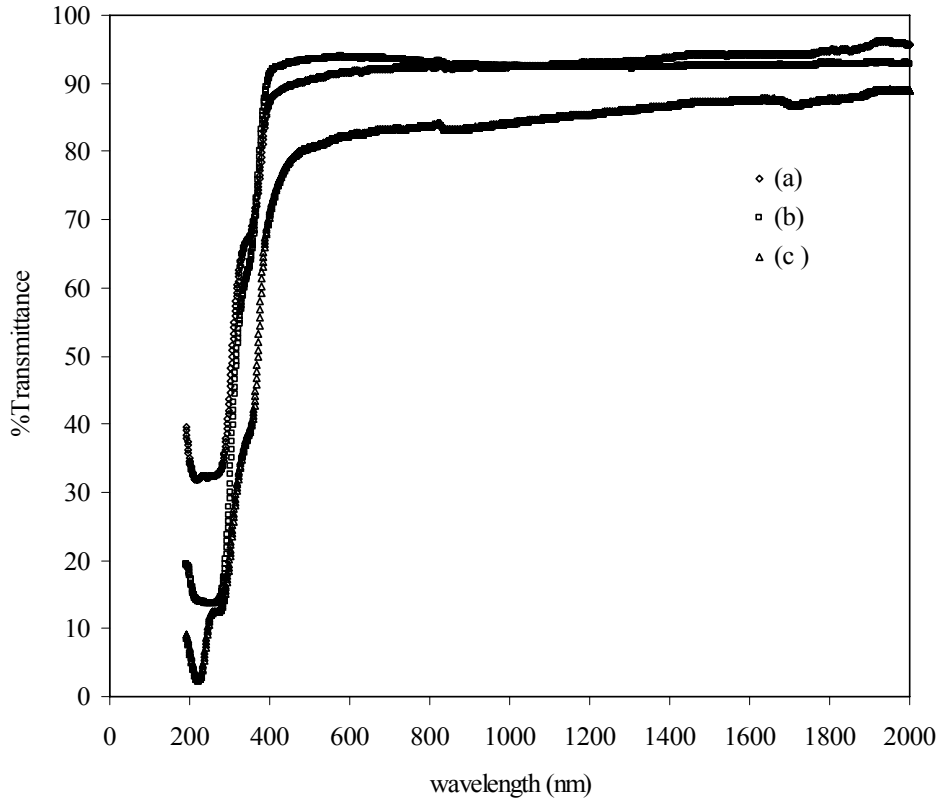


Figure 4 Transmittance spectra of (a) undoped ZnO, (b) 10 wt% AZO and (c) 10 wt% MZO thin films.

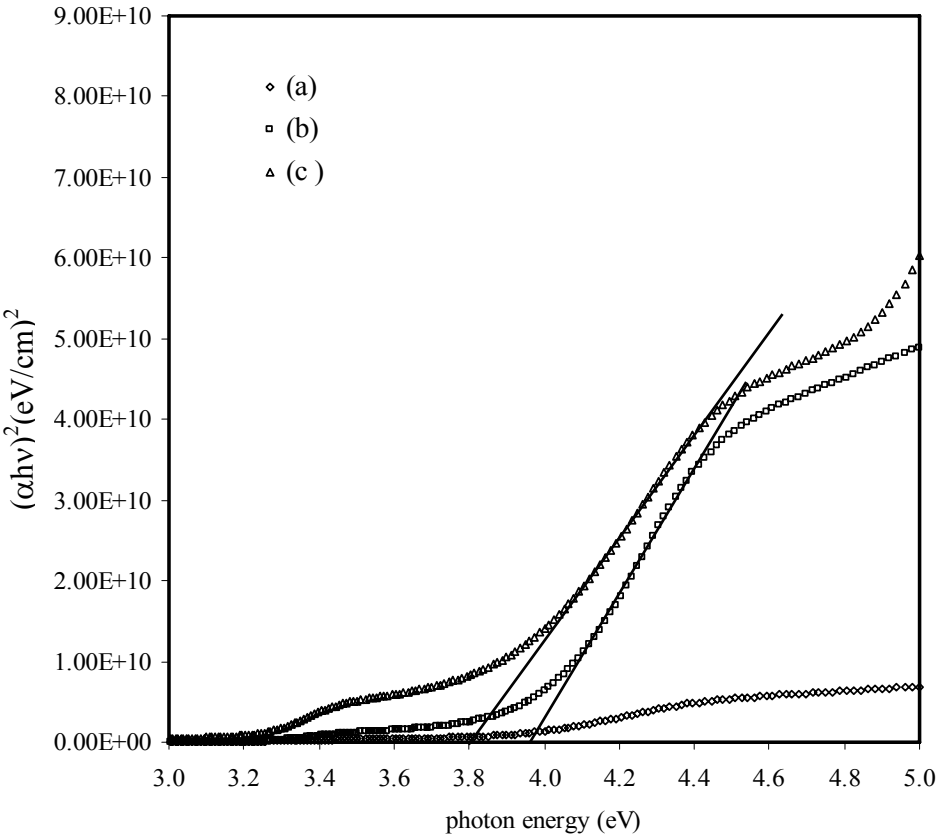


Figure 5 Evaluation of the $(\alpha h\nu)^2$ vs. $h\nu$ curves of (a) undoped ZnO, (b) 10 wt% AZO and (c) 10 wt% MZO thin films.

CONCLUSIONS

In this study, we were successful in preparing ZnO thin films with an average grain size in the nanometer scale via sol-gel dip coating. The c-axis orientation was developed in the case of AZO thin films, but the c-axis orientation was inhibited when doping ZnO with Mn. The Al and Mn ions acted as inhibitors for suppressing the grain growth of ZnO. The average grain size of ZnO from AFM image analysis decreased from 101 nm to 50 and 25 nm when ZnO was doped with 10 wt% Al and 10 wt% Mn, respectively. All thin films gave a transmittance over 80 % in the visible region and band gap values of undoped ZnO, AZO and MZO thin films were 3.24, 3.96 and 3.80 eV, respectively. The increase in the band gap when ZnO was doped with Al and Mn can be explained by the Burstein-Moss effect.

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บทคัดย่อ

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อิทธิพลของสารเจืออะลูมิเนียมและแมงกานีสต่อสมบัติเชิงโครงสร้างและสมบัติเชิงแสงของฟิล์มบางซิงค์ออกไซด์ที่เตรียมจากวิธีโซล-เจล

ฟิล์มบางซิงค์ออกไซด์บริสุทธิ์และที่เจือด้วยอะลูมิเนียมและแมงกานีสปริมาณ 10 wt% ถูกเตรียมบนแก้วด้วยวิธีโซล-เจล แบบการจุ่ม อะลูมิเนียมอิออนแสดงบทบาทสำคัญในการปรับปรุงการโตของฟิล์มในทิศทางแกน c ในขณะที่แมงกานีสอิออนจะขัดขวางการโตของฟิล์มในทิศทางแกน c ขนาดเกรนเฉลี่ยลดลงเมื่อทำการเจือซิงค์ออกไซด์ด้วยอะลูมิเนียมและแมงกานีส ขนาดเกรนเฉลี่ยที่เล็กที่สุดมีขนาด 25 นาโนเมตร ได้จากการเตรียมซิงค์ออกไซด์ที่เจือด้วยแมงกานีสปริมาณ 10 wt% ค่าช่องว่างพลังงานของฟิล์มที่เตรียมได้เปลี่ยนแปลงอยู่ในช่วง 3.24 - 3.96 อิเล็กตรอนโวลต์

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