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ELECTRICAL AND OPTICAL PROPERTIES OF ZnO THIN FILMS GROWN BY R.F. MAGNETRON SPUTTERING FOR SOLAR CELL APPLICATION

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ABSTRACT

Pyramidal textured, good electrical and optical properties of thin films ZnO has been successfully grown by R.F. Magnetron sputtering at low temperature. The grain size of the textured surface is highly dependent on growth condition, especially the special speciments introduced to the system. The pressure was adjusted by flowing the high purity Ar gas into the chamber. The best textured films were obtained by mixing methanol at pressure equal or lower than 15 mTorr. The film thickness are varies from 1μm to 2.5 μm, and having an average total transmittance of 92 - 86 % on the range of 400 to 800 nm wavelength. The films resistivities is lower than 1.5 x 10^{-3} Ωcm, while the haze factor of the best film is about 14.1 %. From XRD measurements, it shows that the textured surface showing four peaks on the direction of (110), (002), (101) and (112), while the non-textured films only show peaks on the direction of (110) and (002).

Keywords: ZnO, electrical and optical properties, thin film, R.F. Magnetron Sputtering.

ABSTRAK

Lapisan tipis ZnO dengan tekstur piramida dengan sifat listrik dan optik yang baik telah berhasil ditumbuhkan dengan menggunakan RF Magnetron Sputtering pada temperatur rendah. Ukuran butiran dari permukaan yang bertekstur sangat tergantung pada kondisi penumbuhan, khususnya pada spesimen yang dimasukkan ke ruang penumbuhan selama pelapisan. Tekanan diatur dengan mengalirkan gas argon murni ke dalam ruang penumbuhan. Lapisan bertekstur yang paling baik diperoleh dengan mencampurkan Methanol ke dalam ruang penumbuhan pada tekanan yang lebih kecil atau sama dengan 15 mTorr. Ketebalan lapisan bervariasi dari 1 sampai 2.5 μm, dan mempunyai harga rata-rata transmissi total 92-86% pada daerah panjang gelombang 400 sampai 800 nm. Resistivitas dari lapisan tipis lebih rendah dari 1.5 x 10^{-3} Ωcm, sementara factor haze untuk film terbaik adalah 14.1%. Dari pengukuran XRD, menunjukkan bahwa permukaan yang bertekstur mempunyai 4 puncak dalam arah (110), (002), (101) dan (112). Sedangkan permukaan lapisan yang tidak bertekstur hanya menunjukkan dua buah puncak dalam arah (110) (dan 002).

***Kata Kunci**: ZnO, sifat listrik dan optik, lapisan tipis, R.F. Magnetron Sputtering.*

INTRODUCTION

There are many problems that the scientists are facing in producing the solar cells, especially to increase the cells efficiency. One of the problems is how to minimize the photon lost from the Sun light due to reflection. One way that one may minimize the lost due to reflection is by manipulating the surface of the materials that one use as the solar cells surface. The highest solar cells efficiency

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(20%) has been obtained by producing the pyramidal surface of the cells surface using the Laser Grooved Buried Contact technique [1]. Zinc Oxide (ZnO) is the oxide that can be produced in the form of thin film with many techniques and also has some interesting applications, such as : sensors and actuators [2], transducer [3], ultrasonic oscillators [4], as the Thin Conducting Oxide (TCO) materials for the solar cell [5] and others. There are many publications have been reported in the growing of ZnO thin films using different techniques, such as photo-MOCVD [6], reactive evaporation [7], spray pyrolisis [8], DC and RF sputtering [9]. As it has been known that the textured surface for the TCO film is very important in the fabrication of the solar cell in order to increase its efficiency, especially for the thin film polycrystalline silicon substrate or even other substrate. T. Nakada et.al [10] had reported that by applying the textured ZnO film into their $CuInSe_2$ thin film solar cells, they have shown that the efficiency increases from 8.85 % (flat ZnO film) to 10.3 % (textured ZnO film).

It is well known that sputtering technique is suitable for low cost and large-scale production of thin film. It has been also long known that the textured ZnO films can be easily obtained using MOCVD technique as has been reported by Wilson *et al* [11]. However using sputtering technique, most of the film surface reported by several groups are flat, and only a few groups that have been reported for the textured ZnO thin film surface. Namely by J.A. Anna *et al*. using RF Sputtering at 150 ^{0}C substrate temperature under H_2O partial pressure in Ar [12], Tokio Nakada *et al*. by DC-Magnetron Sputtering in B_2H_6 -Ar Mixtures [13] and also in the H_2O partial pressure [14] at the substrate temperatures equal or higher than 200^{0}C.

In this paper we report on the electrical and optical properties of the ZnO thin film grown by RF Magnetron Sputtering to be match with the need of the solar cells application.

EXPERIMENTAL WORK

The growth process was done using a 10 cm disk ceramic type of ZnO:Al doped (98 % ZnO and 2 % Al_2O_3), while the substrates were 5 cm x 5cm 7059 Dow Corning glass. The substrate temperature that was used for growing the textured surface ZnO is around 100^{0}C, which is the lowest substrate temperature that ever reported.

In order to obtain a textured surface, a few drops of water or Methanol were introduced to the deposition chamber. After inserting the substrate, the system was pumped down until the pressure has reaching about 10^{-6} Torr, then the substrate temperature was increased to 100^{0}C. Hence high purity Ar gas was introduced to the chamber so that the deposition pressure during experiment can be adjusted. The RF Power during deposition was kept at 250 Watt. The deposition time for this experiment was about 2 hours long. The film thickness were measured by an Alpha-Step 200 stylus profilometer-

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Tencor Instruments. The total and diffused transmittance was measured using Shimadzu UV-3101PC spectrophotometer, the grain size by SEM measurements, the electrical properties such as film's resistivity, mobility and carrier concentration were measured using Lake Shore 7500 series Hall System measurements, and the structural properties was measured by x-ray diffraction.

Graphite disk placed on top of the glass substrate has two functions at this experiment. First, it is used as the substrate plate heater, so its temperature will not be fluctuated too far from the set value. Second, it is used as the water or methanol carrier to the system. Water or methanol is dropped a few drops to the graphite before inserting the substrate into the system. When the temperature is increased to the set value prior and during the deposition, then water or methanol will be vaporized from the graphite into the chamber atmosphere. Then the chemical reaction will occur between the water or methanol vapour with the ZnO molecule or O atom in the forming of ZnO Film on the glass substrate. Figure 1 is the schematic diagram of the main equipment of the deposition system.

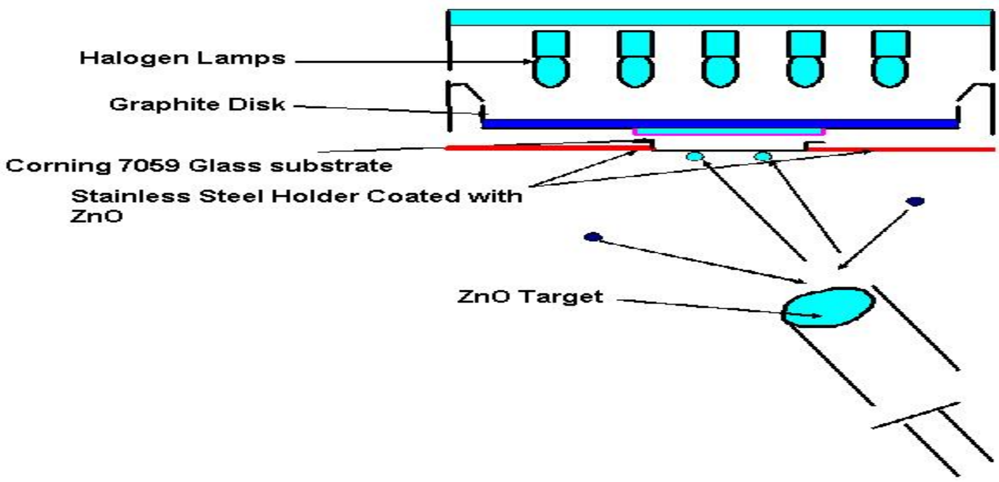

Figure 1. The schematic diagram of the main equipment of the R.F. Magnetron Sputtering deposition system.

RESULTS AND DISCUSSIONS.

SEM Measurements

SEM photographs (top view) of all samples that are named with MZNO as prefix followed by numbers such as MZNO: 6, 30, 31, 57 and 58 are given in Figure 2. Actually, MZNOs here are the sample names of ZnO films. The SEM side view of the samples is given in Figure 3. Then the other properties and growth condition are given in Table 1.

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From Figure 2, it can be seen that samples MZNO: 6, 30 and 31 show very clear pyramidal structures, while sample MZNO-57 only shows a bit of the pyramidal structure with a high number of porosity. However, sample MZNO-58 shows more likely polycrystalline structure.

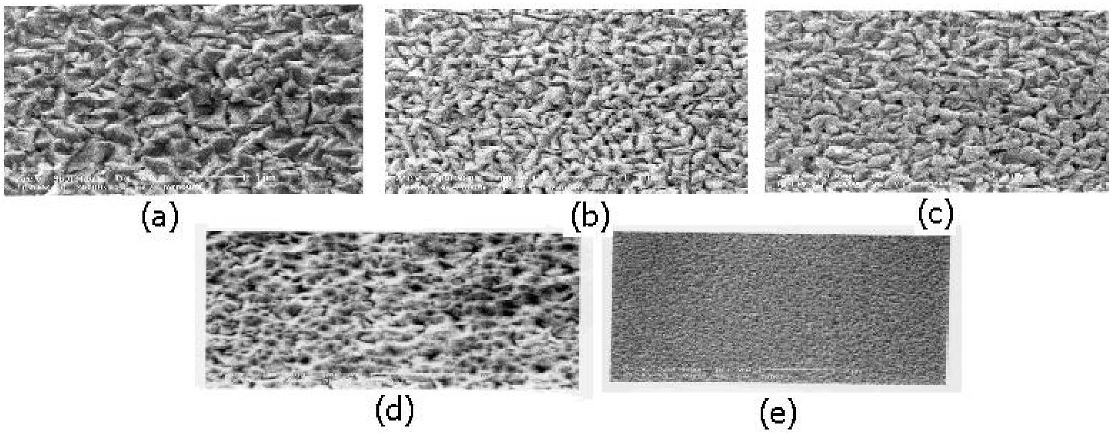

Figure 2. SEM photographs of Samples (Top View) (a) MZNO-6, (b) MZNO-30, (c) MZNO-31, (d) MZNO-57 and (e) MZNO-58.

If one pays close attention to Figure 2 and Figure 3, for an example, it is clearly seen that larger grain size (Figure 2a) is also supported by the growth of ZnO starting from small size on the glass substrate and becomes larger on the surface (Figure 3a). Another example, the surface that is not showing the pyramidal texture (Figure 2e) is due to the growth of the ZnO on the glass surface is in the form of needle structure (Figure 3e).

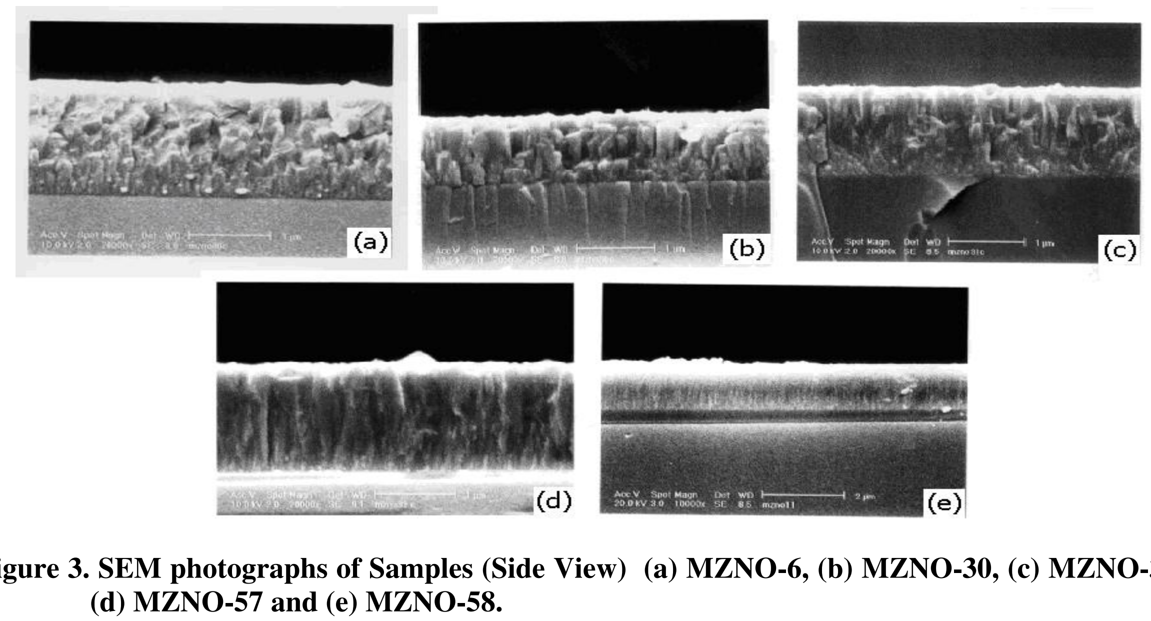

Figure 3. SEM photographs of Samples (Side View) (a) MZNO-6, (b) MZNO-30, (c) MZNO-31, (d) MZNO-57 and (e) MZNO-58.

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We believe that the pyramidal textured surface of the films is due to Hydroxide molecule (OH) that appears during films deposition, since none of the films showing such surface without introducing a small amount of water (H_2O) or Methanol (CH_3COOH) to the system, as can be seen in Table 1 for sample MZNO-58. The same OH molecule effect that responsible for the ZnO textured surface had been claimed by Tokio Nakada *et al* [13]. As their prove, during the growth process they also measured the emission spectra at the position near the ZnO target in the presence of plasma. As the result they found that there is also the form of OH molecule in the gas phase when they use a mixture of Ar and H_2O. While on the deposition using pure Ar they did not observe the appearance of OH molecules.

In our system we have no facility in observing the OH molecule during the deposition. However, the result that Tokio *et al* had obtained, and the result that we are showing in this paper is quite agreeable to each other. So, during the deposition process, the molecule of OH is formed on the gas phase, and these molecules precipitate into the substrate and growing together with ZnO.

This effect also explain why in our films using methanol (CH_3COOH) always showing a little bit better textured quality compare with our films using water (H_2O), since by using CH_3COOH during deposition, there are more OH molecules present on the system compared with using H_2O.

As also suggested by Tokio *et. Al.,* there are two possible sources of OH molecules in our system. Such as; (1) the direct reaction of the decomposed O from ZnO with H from H_2O or CH_3COOH and (2) OH molecules from the decomposition of H_2O or CH_3COOH. However the amount of OH molecules may be different in our system, since we only introduced a certain amount of water or methanol to the system together with the substrate, so that its number is changing during the growth process. This is also the reason why the grain size of the pyramidal textured surface of the films are vary for each growth, since we have no control in introducing the same amount of H_2O or CH_3COOH to the system.

Electrical Measurements

The electrical properties of the films, such as resistivity, carrier mobility and carrier concentration are measured using Lake Shore 7500 series Hall System measurements and the results are presented at Table 1 for five samples that were thoroughly studied.

As can be seen from Table 1, the resistivity of films are not vary too much, which is around 0.6×10^{-3} to 1.4×10^{-3} Ωcm. Also the carrier concentration of the films varies from $2.89 \times 10^{20} cm^{-3}$ to $4.11 \times 10^{20} cm^{-3}$. However the mobility of the carrier for the different pyramidal textured films very dependent on the grain size of the films. As it can be seen from Table 1 for the pyramidal texture

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surface (Fig. 1: a, b and c), sample MZNO-6 which has the largest grain size has the mobility twice of the mobility for the sample MZNO-30 which has the smallest grain size.

Table 1. The ZnO Films Characteristics.

Sample	Pres (mTorr)	Thick (μm)	ρ x 10^{-3} Ωcm	μ (cm^2/V.s)	n $10^{20}cm^{-3}$	h (%) at 400 nm	Growth Condition
MZNO-6	5	1.6	1.12	28.7	3.16	14.1	Methanol
MZNO-30	50	1.0	1.08	14.0	4.11	8.6	Methanol
MZNO-31	15	1.3	1.40	15.4	2.89	9.0	Methanol
MZNO-57	10	1.6	.633	27.8	3.55	13.1	Water
MZNO-58	10	1.55	1.23	22.6	2.25	8.4	None

The mobility of samples MZNO-57 is still high although the structure is not perfectly pyramidal. This can still be acceptable since as one can see from Figure 1(d) that some of the grains size of the film is still compatible with sample MZNO-6. However, it is still not clear what makes that the mobility of sample MZNO-58 is high enough although its structure is more likely such polycrystalline structure. One possible explanation that we may give for this case is that the carrier may not flow laterally through the film, but it flows vertically downward through the thickness of the film and then flow at the bottom (border with substrate), then finally again flow vertically upward through the thickness of the film to the probe of the stylus meter on the other side of the film surface. This phenomenon may be true, since the film seems to grow from the bottom to the top surface more likely such needle type. In this case, when carriers flow, they will face much lower resistance, rather then flowing horizontally from one probe to the other on the film surface. This possibility may be accepted if one can see how the side view of the sample MZNO-58 look likes in Figure 2 (e). It is very different with other four samples (Fig 2: a, b, c and d), where the grain size of the film is clearly seen growing bigger from the bottom to the surface. With other words, the grain size at the bottom surface much-much smaller than on the top surface of the film. So that the carrier will have less resistance to flow laterally on the film surface rather than the way that we suspected occur for sample MZNO-58.

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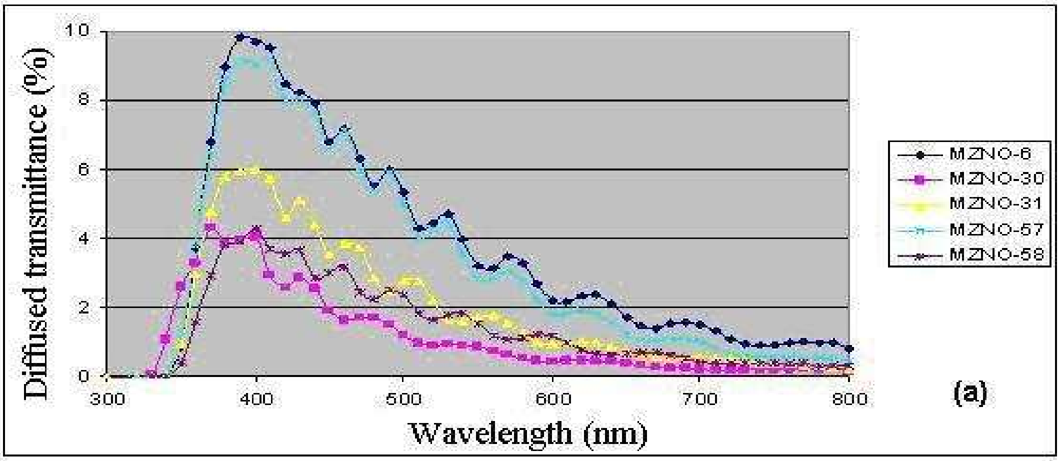
Optical Measurements.

The total and the diffused transmittance of the five samples that are discussed in this paper are given in Figure 4. As can be seen from Figure 4 (a) and also Table 1, the best films have the haze factors of about 14.1 % and 13.1% consecutively for sample MZNO-6 and MZNO-57.



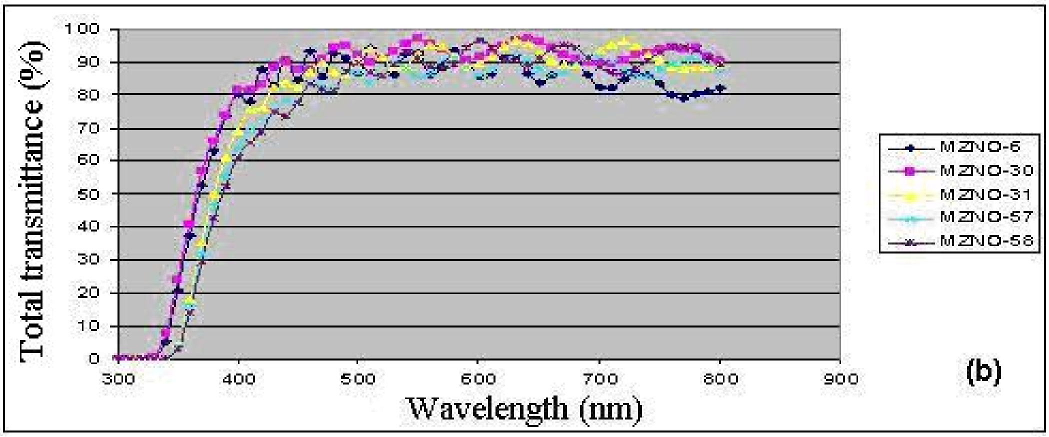


Figure 4. The Total and the Diffused transmittance of the textured ZnO Films: (a) Diffused transmittance (b) Total transmittance.

We can see that the MZNO-6 has the best pyramidal texture quality, and the biggest grain size which is about 0.5 to 0.75 μm with films thickness varies from 1 μm to 2.5 μm, and having an average total transmittance of 86-92 % (only about 6-10% difference) on the range of 400 to 800 nm wavelength (Figure 4.b). This value is still considerable quite high enough for the use as the TCO film in the solar cell application.

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Again if one looks at Figure 4 (a), the diffused transmittance of sample MZNO-6 is almost similar to that of MZNO-57 (only about 1% difference). This shows that the grain size and the shape of the grain films are quite similar, even sample MZNO-57 seems to be more porous than sample MZNO-6, but the ability of diffusing light not much different. But for sample MZNO-58, according to the grain size that are shown in Figure 2 and Figure 3, the diffused transmittance of sample MZNO-58 should be the smallest one. However, if one looks more closely to the needle shape of sample MZNO-58 grains, it is still able to diffuse light and slightly better than sample MZNO-30 which has larger grain size.

XRD Measurement

The XRD pattern of the five samples that are discussed in this paper are shown in Figure 5. Except sample MZNO-58 which has only two strong peaks in the direction of (100) and (002) as usual, and a weak peak in the direction of (112), all other samples showing four peaks in the direction of (100), (002), (101) and (112), which means that the films has a good textured, and the growth is the granular form. The strong peak on the (002) direction for all the films shows that the growth is mainly on the c axis of the ZnO structure, and it is perpendicular to the glass substrate. Contrary, again if one looks at sample MZNO-57, the peak on the (101) direction is quite weak, while for sample MZNO-58 there is no peak at all appear on that direction. This coincides with the SEM photographs of the samples in Figure 2 and Figure 3 which have not showing the pyramidal growth as other samples do.

CONCLUSION

The electrical and optical properties of the films are very dependent on the grain size of the textured surface of ZnO. The best textured film was obtained by mixing methanol to the system at pressure equal or lower than 15 mTorr. The ZnO film resistivity is lower than 1.5×10^{-3} Ωcm, while the haze factor of the best film is about 14.1%. The films thicknesses vary from 1 μm to 2.5 μm, and having an average total transmittance of 86-92% in the wavelength range of 400 to 800 nm. XRD measurements show that the textured surface showing four peaks on the direction of (110), (002), (101), and (112), while for non-textured surface films only show peaks on the direction of (110) and (002). From the films properties that were obtained, although it has not been tested, the ZnO films grown by RF Sputtering are very promising as anti reflecting films for solar cells application.

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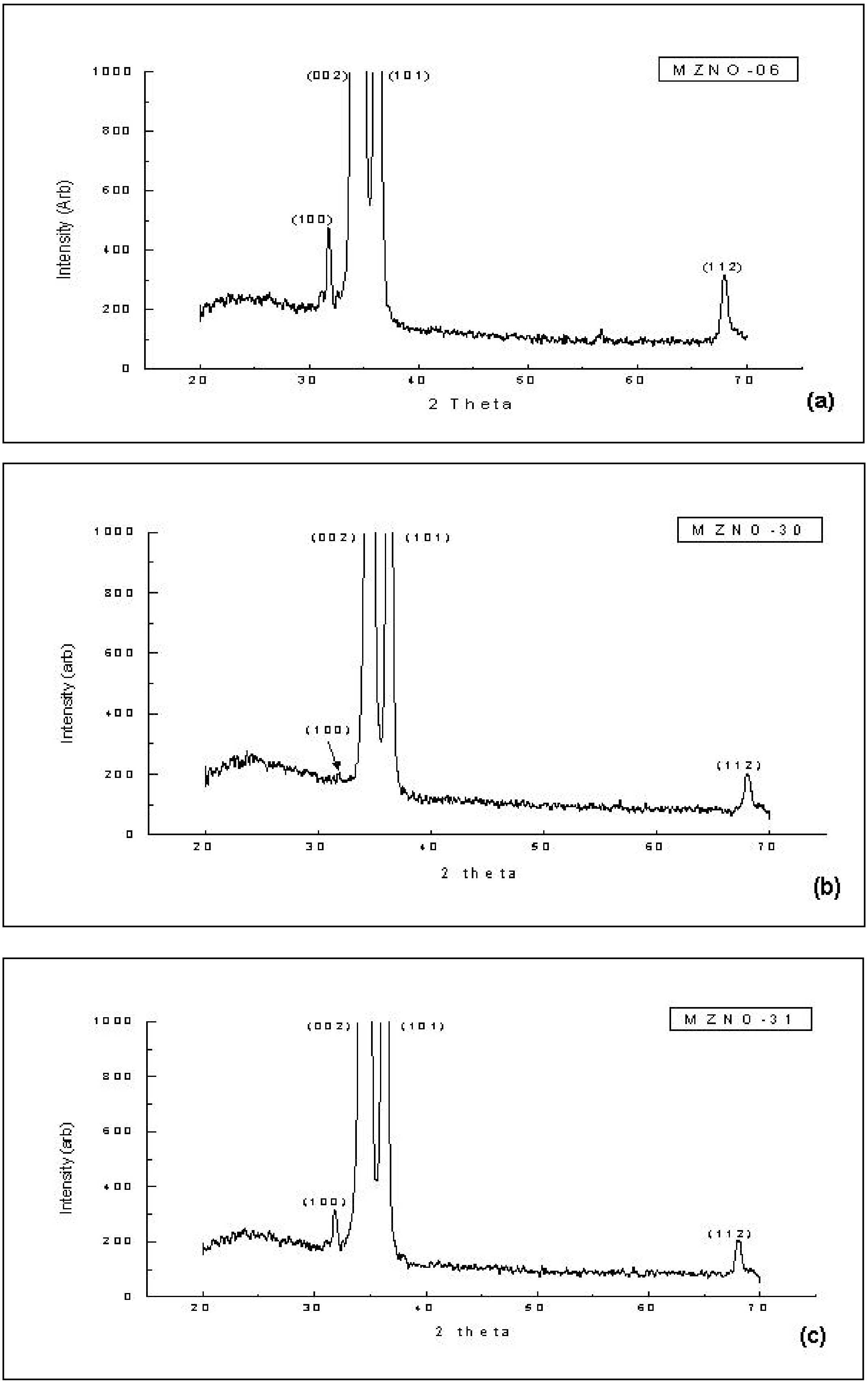

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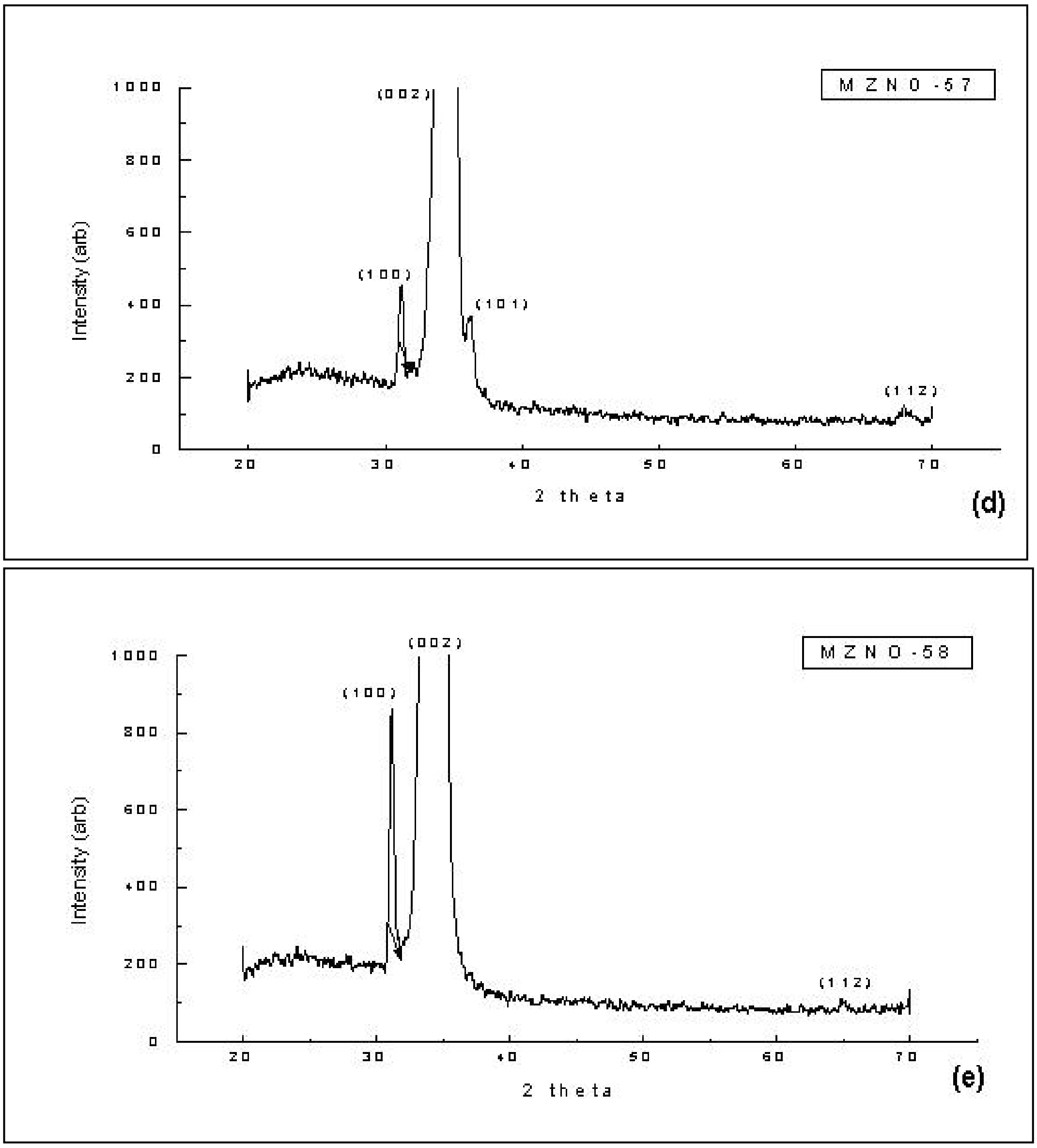

Figure 5. The XRD pattern of the five samples: (a) MZNO-6, (b) MZNO-30, (c) MZNO-31, (d) MZNO-57 and (e) MZNO-58.

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