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Mikroskop camları üzerinde spin kaplama yöntemiyle üretilmiş ZnO ince filmlerine tavlama sıcaklık ve süresinin etkileri

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ÖZET

Bu çalışmada, amorf mikroskop camlar üzerine spin kaplama yöntemi kullanılarak ZnO ince filmleri üretilmiş ve bu filmler 350 ^{o}C ile 850 ^{o}C arasında değişen sıcaklıklarda tavlanmışlardır. Tavlamalar 50 ^{o}C'lik aralıklarla gerçekleştirilmiş ve iki farklı (0.5 ve 8 saat) tavlama süresi kullanılmıştır. Bütün numunelere ait XRD, SEM ve UV-Vis spektrumları alınarak numunelere ait optik ve yapısal özellikler analiz edilmiştir. 400 ^{o}C'de sekiz saat tavlanan numunede sadece (100) yönünde kristallenme gözlenmiştir. 800 ^{o}C ve 850 ^{o}C tavlamaları SiO_2 ve Zn_2SiO_4 ile bağlantılı iki faz üretmiştir. Yapılan deneyler tavlama sıcaklığı ve süresinin genelde ZnO nanoyapılarının çaplarını artırdığını göstermiştir. Orta sıcaklıklarda (350-600 ^{o}C) tavlanan numunelerde 370 nm'de (3.36eV) konuşlanmış bir soğurma bandı gözlenirken bu pik 650 ^{o}C'den sonraki tavlama sıcaklıklarında 290 nm'de yeni bir soğurma piki oluşturmuş ve bu yeni pikin de SiO_2 fazından kaynaklandığı tespit edilmiştir. 800 ^{o}C'de 8 saat tavlanmış numunelerde SiO_2 soğurma pikinde 10 nm'lik bir kırmızaya kayma tespit edilmiştir.

Anahtar Kelimeler: ZnO ince filmler, spin kaplama, ısıl tavlama, mikroskop cam, optik spektrum

Effects of thermal annealing temperature and duration for ZnO thin films produced by spin coating method on microscope glasses

ABSTRACT

In this study, ZnO thin films on amorphous microscope glasses were fabricated using the spin coating method and annealed at temperatures ranging from 350 ^{o}C to 850 ^{o}C. Annealings have been performed at these temperatures in 50 ^{o}C increaments and for two annealing durations (0.5 and 8 hours). XRD, SEM and UV-VIS spectra of all the samples have been given. Optical and structural properties of the produced films have been evaluated. The sample annealed at 400 ^{o}C for eight hours was crystallized in only one (100) direction. Annealing at 800 ^{o}C and 850 ^{o}C created new phases related to SiO_2 and Zn_2SiO_4, respectively. It has been found that the annealing temperature and duration generally increased the ZnO nanostructures' diameter. The UV-VIS spectra of the samples for moderate temperatures (350-600 ^{o}C) had an absorption band at 370 nm (3.36eV), whereas these peaks disappeared after 650 ^{o}C annealing, producing a new absorption peak situated at 290 nm which could be attributed to the SiO_2 phase. In case of the sample annealed at 800 ^{o}C for 8 hours, SiO_2 absorption peak has 10 nm redshift.

Keywords: ZnO thin films, spin coating, thermal annealing, microscope glasses, optical spectra

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1. INTRODUCTION (GİRİŞ)

Especially in the last two decades, nanosized structures have attracted great attention owing to their novel size-dependent applications in the area of photonics [1-4]. Amongst the metal oxides, zinc oxide is of importance in the scientific research area due to its unique properties and its compatibility to the electronic and optoelectronic devices. It has good electrical properties, high luminescence yield, high transmittance constant in the visible region, excellent substrate adherence and low price [5]. It can be used as photo-catalyzers, field-effect transistors, UV light emitting diodes, varistors, solar cells, chemical/gas sensors, antimicrobial staff, as well as feeding agents [6-12]. Zinc oxide is a direct bandgap (~3.37 eV) semiconductor material and it has exciton binding energy of 60 meV, which is larger than GaN (28 meV) and ZnSe (19 meV) [13]. It has a stable wurtzite structure with the lattice spacings of a = 0.325 nm and c = 0.521 nm.

Producing ZnO thin films is an active field (published ~5500 papers/year). These films have been prepared by various dry and wet processes, such as metal organic chemical vapor deposition (MOCVD), chemical vapor deposition (CVD), pulsed laser deposition (PLD), molecular beam epitaxy (MBE), magnetron sputtering, electrochemical deposition, spray prolysis etc. [14,15]. Hydrothermal film preparation procedure is also used to prepare these oxide films.

Sol-gel chemistry has become a famous tool to make new kind of thin films and combining this with the spin coating method provides excellent film qualities, which consequently satisfies all the requirements that the user wants to fulfill. This method is very easy to implement and cheaper than the others. With this technique some tens of cm^2 film areas can be produced on both the crystalline and the amorphous surfaces. Crystallization temperature for these films can be as low as 300 ºC under normal conditions. The crystalline quality of the film can be improved by the conventional annealing processes [16-17].

In this study, thermal treatment results in terms of annealing temperature and duration for the ZnO thin films on amorphous microscope glasses have been introduced. The effects of annealing temperature and duration on the samples have been investigated by using XRD, SEM and UV-Vis absorption spectra, and the results have been interpreted.

2. EXPERIMENTAL (DENEYSEL)

ZnO thin films were deposited onto microscope glasses using spin coating method. Zinc precursor solution was prepared by dissolving zinc acetate dehydrate ($C_4H_{10}O_6Zn$) in methoxyethanol ($C_3H_8O_2$) to obtain 0.33 M concentration. In the process, monoethanolamine was used as a complexing agent in order to keep the metal ions in the homogenous solution with no precipitation. The solution was mixed at 70 ºC/1 h using magnetic stirrer (Wisestir, MSH-20A) at atmospheric pressure. The thin films were spin coated on microscope glasses at the speed of 500 rpm. One layer deposition took 40 second and ten layers of deposition have been performed. After each layer formed, the films were dried at 250 ºC for 10 minutes, the thin film coated samples were finally annealed at various temperatures from 350 ºC to 850 ºC for half an hour and eight hours periods at a furnace (Nabertherm B170). For these two distinct annealing durations we have prepared the samples in pairs and the annealings have been performed individually to see the annealing time effects on the mechanical and/or optical properties (see Figure 1.).

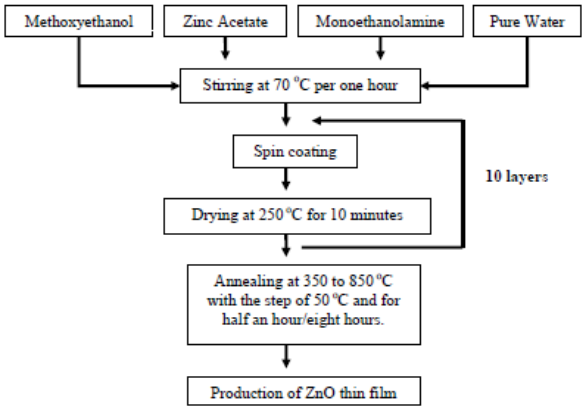

Figure 1. Flow diagram of ZnO thin film production process (ZnO ince film üretim sürecinin akış diyagramı)

XRD spectra of the sol-gel films have been recorded by means of XRD diffractometer Rigaku D/Max 2200PC using CuK_α band.

Absorbtion measurements of the samples have been performed by using Agilent 8453 UV-VIS spectrometer. In these measurements, white light has been sent onto the samples' coated and uncoated faces and the absorption spectra have then been taken to see whether diffusion and other physical processes are present and have any consequences on the mechanical and/or optical properties or not. These two spectra for all the samples have been evaluated. Surface morphology of the ZnO thin films were observed using SEM (JEOL 6060LV).

3. RESULTS AND DISCUSSION (SONUÇLAR VE TARTIŞMA)

3.1 XRD Spectra

The XRD spectra of the samples, which were annealed at 350 to 850 ºC for half an hour/eight hours, have been performed using Rigaku D/Max 2200 PC XRD spectrometers CuKα band. It has been observed that all the samples were crystallized at these temperatures and annealing durations. An XRD spectrum for the sample which was annealed at 450 ºC for eight hours is shown in Figure 2.

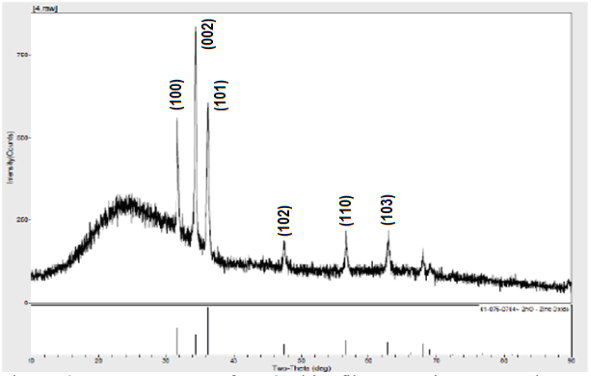

Figure 2. XRD spectra of ZnO thin film on microscope glasses, annealed at 450 ºC for eight hours (450 ºC'de 8 saat tavlanmış mikroskop gözlük üzerindeki ZnO ince film XRD spektrumları).

Surprisingly, for the sample annealed at 400 ºC for eight hours the two of the three main conventional ZnO peaks (see Figure 3-b) have disappeared and one remained, showing that the crystal growth has occurred in (100) preferred direction. This was not the case for the sample annealed at the same temperature for 30 minutes (Figure 3-a).

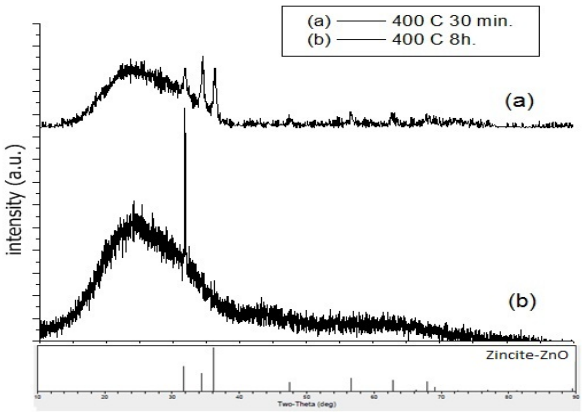

Figure 3. XRD spectra of the ZnO thin film annealed at 400 ºC for a) half an hour and b) for eight hours (a) 400 ºC'de yarım saat b) sem.z saat tavlanmış ZnO ince filmin XRD spektrumu).

For the samples annealed at the temperatures ranging from 450 ºC to 750 ºC there exist no differences than that of the conventional XRD spectra. However, for the 800 ºC annealings it has been observed that all the classical peaks have disappeared and a peak at the angle of 25º (2θ) come up (see Figure 4-a).

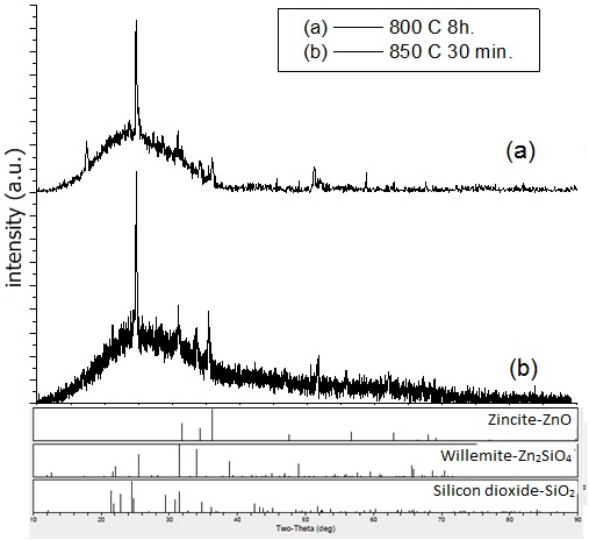

Figure 4. XRD spectra of ZnO thin film coated on microscope glass and annealed a) at 800 ºC for 8 hours and b) at 850 ºC for 30 minutes (a) 800 ºC'de 8 saat veb) at 850 ºC'de 30 dakika tavlanmış mikroskop camı üzerine kaplanmış ZnO ince film XRD spektrumları).

This peak is attributed to the SiO_2 (quartz) crystal phase. To understand the origin of this peak, i.e., whether it comes from the substrate (which was amorphous SiO_2) or it originates from the produced ZnO thin film, we have carried out another experiment with non-coated microscope glasses for the same experimental conditions and saw no sign for crystallization. This showed us that the SiO_2 peak at the XRD spectrum was caused by the ZnO thin film coating. This peak shows the mutual interaction of ZnO and substrate (SiO_2), which produces SiO_2 crystal phase, silicon coming from the substrate and oxygen contributing from the coated thin film. For the ZnO spin coated sample annealed at 850 ºC for 30 minutes there appeared another phase, called willemite (Zn_2SiO_4) (see Figure 4-b). In this spectra three main ZnO peaks show themselves, though weak. Since the substrate was amorphous silica and the temperature (850ºC) was over the softening point, we could not go further than this temperature. However, it was believed that the increasing the temperature produced new, intermediate phases related to the ZnO thin films and substrate which was in the current case SiO_2 for 800 ºC and Zn_2SiO_4 for 850 ºC annealings.

3.2 SEM Spectra

The SEM spectra of all the samples have been taken using SEM (JEOL 6060LV) spectrometer. From the spectra it has been found that the average thicknesses of the films were about 1μm.

From the SEM micrographs, it has been also realized that increasing the annealing temperature generally increases the ZnO nano-microstructures' diameter and length to some extent. Duration of the annealing (0.5 – 8 h) did not change the shape of the structures much. For the higher annealing temperatures (700-850 ºC), spacings between the grains have become smaller and production of bigger sized structures occurred. For the samples which were annealed at 400 ºC for half an hour and eight hours, the SEM spectra showed distinct properties (see Figure 5). As mentioned in section III.a, the XRD spectra showed a preferential growth mechanism. The ZnO nanostructures at this temperature for 8 hour annealing were grown in different manner. As could be seen from Figure 5-a the ZnO nanostructures seemed to be rod-like, whereas for 8 hour annealing these occurred to be homogenous, dot-like (nanodot) structure with the average diameter of 500 nm (see Figure 5-b).

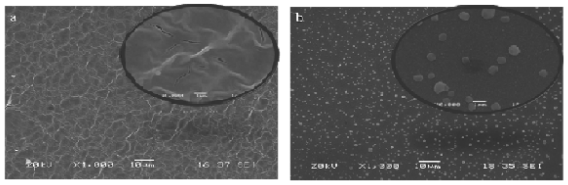

Figure 5. SEM micrograph of the samples annealed at 400 ºC for a) half an hour and b) 8 hours (a) 400 ºC'de yarım saat b) sekiz saat tavlanmış numuneler için SEM mikrografisi).

The dotted structure slowly diminishes for the 450-500 ºC annealings (see Figure 6).

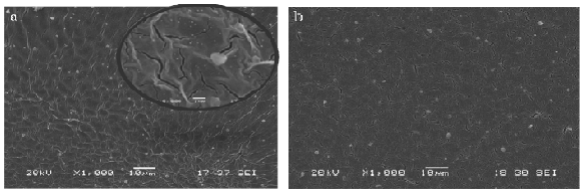

Figure 6. SEM micrograph of samples annealed at a) 450 ºC for eight hours b) 500 ºC for half an hour (a) 450 ºC'de sekiz saat b) 500 ºC'de yarım saat tavlanmış numuneler için SEM mikrografisi).

This structure completely disappeared after 550 ºC annealing for both annealing durations (see Figure 7), and nanorods length became longer for higher annealing temperatures (for example see Figure 8, for 600-650 ºC annealing).

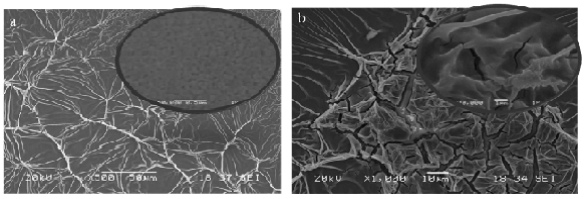

Figure 7. SEM micrograph for the samples annealed at 550 ºC for a) half an hour b) eight hours (550 ºC 'de tavlanmış numuneler için SEM mikrografisi a) yarım saat b) sekiz saat)

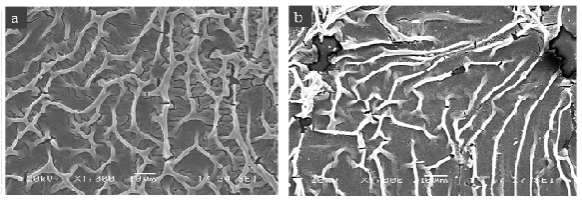

Figure 8. SEM spectra for the samples annealed at a) 600 ºC for half an hour; b) annealed at 650 ºC for half an hour (600 ºC'de a) yarım saat; b) 650 ºC'de yarım saat tavlanmış numuneler için SEM spektrumu).

At higher annealing temperatures (700-850 ºC), the rod-like structure disappeared while the dot like structure dominated and the grains of dots became bigger, reaching diameters of up to 50 nm (see Figure 9).

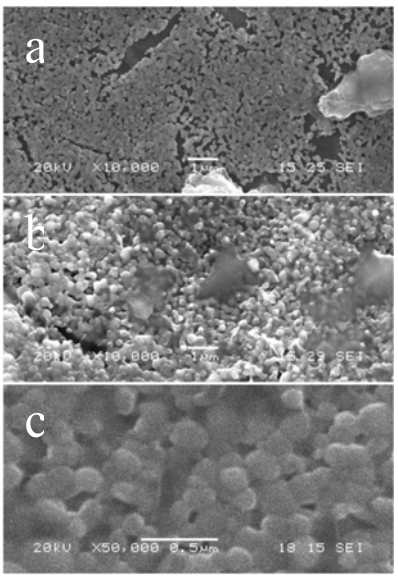

Figure 9. SEM spectra of the samples annealed at a) 700 ºC for 8 hours b) 800 ºC for 8 hours c) 850 ºC for 30 minutes ((a) 700 ºC'de 8 saat b) 800 ºC'de 8 saat c) 850 ºC'de 30 dakika tavlanmış örneklerin SEM spektrumu).

3.3 UV-Vis Absorbtion Spectra

Absorption spectra of the ZnO thin films coated on microscope glasses have been obtained by using Agilent

8453 UV-VIS spectrometer. Even though the spectra have been taken between 280 nm to 800 nm we have focused on the wavelength interval of 300-450 nm to see whether there is any shift in the fundamental absorption peak which lies on about 370 nm (3.36 eV). These spectra have been taken for both coated and uncoated surfaces of the substrate (sending white light from these sides and detecting the signal from the other faces) to see any diffusion effect during the annealings. For the annealings from 350 to 600 ^{o}C the absorbtion spectra of all the samples (for 30 minutes and eight hours annealings) were more or less similar, as was depicted in the Figure 10-a.

After 650 ^{o}C annealing the absorption spectra changed completely; the peak at 370 nm disappeared and a peak at about 290 nm became apparent which could be attributed to the SiO_2 absorption band. These changes were in good agreement with the XRD spectra of the samples in which a new phase of SiO_2 were very apparent in, for example, 800 ^{o}C and 850 ^{o}C annealings. Another interesting thing in the absorption spectra was that for the 800 ^{o}C annealing (for 8 hours) there existed a red shift, which was about 10 nm, in the SiO_2 peak and this shift could be attributed to the diffusion effect of SiO_2 nanoparticles or to the bigger grain sizes which might be developed on the substrate as the base layer on which the second layer was formed (see Figure 10-b). As the layers became thicker the upper layers' grain sizes might in general be smaller than those of the first one.

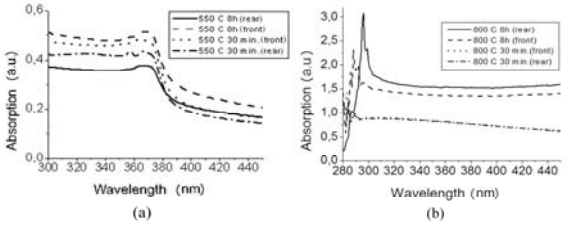

Figure 10. Absorption spectra of ZnO thin films annealed a) at 550 ^{o}C b) at 800^{o}C (ZnO ince filmlerin absorpsiyon spektrumları a) 550 ^{o}C b) 800^{o}C) .

4. CONCLUSIONS (SONUÇLAR)

In this study ZnO thin films were fabricated using the spin coating method and their optical and structural properties were investigated for various annealing temperatures and annealing durations. It has been found that the annealing at 350 ^{o}C created crystallinity of the ZnO film and increasing the annealing temperature changed the structural and optical properties to some extent. The sample annealed at 400 ^{o}C for eight hours showed an interesting profile, where ZnO thin film was crystallized in only one (100) direction. Up to 600 ^{o}C, annealing the samples showed conventional XRD peaks of the ZnO thin films. Above this temperature, the XRD results imply that the amorphisation may occur in the films. However, annealing at 800 ^{o}C improved a new phase, related to the SiO_2 crystal and this phase become Zn_2SiO_4 for 850 ^{o}C annealing, except that the conventional ZnO peaks came back, even though their intensities were weak.

From the SEM micrographs it has been found that the films have a thickness of 1 μm and increasing the annealing temperature and duration generally increased the ZnO nanostructures' diameter. After 400 ^{o}C annealing, the ZnO nanorods started to disappear resolving themselves to more homogenous structures (nanodots), which have the diameter of 500 nm. This figure slowly changed to dot-rod like structure for 450-500 ^{o}C annealing temperatures. The samples annealed at 550 ^{o}C and 600 ^{o}C showed the nanorod-like structures. For higher annealing temperatures (700-850 ^{o}C) the rod-like structure more or less killed off and homogenous film was obtained, with the grain size of 50 nm.

The UV-VIS spectra of the samples for moderate temperatures (350-600) have an absorption band at 370 nm (3.36eV), whereas after 650 ^{o}C annealing these peaks disappear, producing a new absorption peak situated at 290 nm which can be attributed to the SiO_2 phase. This result is in good accordance with our XRD result as well. For the sample annealed at 800 ^{o}C for 8 hours the SiO_2 peak has 10 nm redshift.

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