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H_2 Gas Response of NiO Thin Film at Different Gas Concentrations

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Abstract: Interest in H_2 energy, which is one of the alternative energy sources that can meet the energy needs of the increasing world population, is increasing day by day. However, dangerous properties of H_2 gas such as high flammability and explosiveness require sensitive detection of this gas. For this purpose, intensive research is being carried out on the detection of H_2 gas with high response values at low gas concentrations. In this study, the structural, morphological and H_2 gas sensing characteristics of NiO thin film, which grown on quartz substrate by RF sputtering. XRD results of the produced film revealed that the NiO film has a polycrystalline cubic structure with (101), (012), (110) and (113) diffraction planes. The lattice constant of the film was obtained as 4.226 nm, which differed by 1.274% from the theoretical values presented in the literature. From the special scanning XPS spectrum of the Ni element, the presence of peaks corresponding to Ni^{+2}, Ni^{+3} and NiOOH on the film surface was detected. SEM images revealed the existence of a homogeneous structure on the film surface consisting of structures with grain sizes of 10-20 nm. Current changes obtained at 100, 500 and 1000 ppm H_2 concentrations at 300°C showed that the produced film was sensitive to H_2 gas and the current value increased as the ppm value increased. For 1000 ppm H_2, the response value was 11.49, the response and recovery times were 239 and 286 seconds, respectively. Gas sensor measurements have also shown that the NiO film produced may have p-type conductivity.

NiO İnce Filmin Farklı Gaz Konsantrasyonlarında H_2 Gazı Tepkisi

Anahtar Kelimeler
NiO,
XRD,
XPS,
H_2,
Gaz sensör

Öz: Artan dünya nüfusunun enerji ihtiyacını karşılayabilecek alternatif enerji kaynaklarından biri olan H_2 enerjisine olan ilgi her geçen gün artmaktadır. Ancak H_2 gazının yüksek yanıcılık ve patlayıcılık gibi tehlikeli özellikleri bu gazın hassas bir şekilde tespit edilmesini gerektirmektedir. Bu amaçla düşük gaz konsantrasyonlarında yüksek tepki değerlerine sahip H_2 gazının tespiti üzerine yoğun araştırmalar yürütülmektedir. Bu çalışmada RF sıçratma yöntemiyle kuvars alttaş üzerinde büyütülen NiO ince filmin yapısal, morfolojik ve H_2 gazını algılama özellikleri incelenmiştir. Üretilen filmin XRD sonuçları, NiO filminin (101), (012), (110) ve (113) kırınım düzlemlerine sahip çok kristalli kübik bir yapıya sahip olduğunu ortaya çıkardı. Filmin örgü sabiti 4,226 nm olarak elde edildi ve bu değer literatürde sunulan teorik değerlerden %1,274 farklılık gösterdi. Ni elementinin özel taramalı XPS spektrumundan film yüzeyinde Ni^{+2}, Ni^{+3} ve NiOOH'ye karşılık gelen piklerin varlığı tespit edildi. SEM görüntüleri, film yüzeyinde tane boyutları 10-20 nm olan yapılardan oluşan homojen bir yapının varlığını ortaya çıkardı. 300°C'de 100, 500 ve 1000 ppm H_2 konsantrasyonlarında elde edilen akım değişimleri, üretilen filmin H_2 gazına duyarlı olduğunu ve ppm değeri arttıkça akım değerinin arttığını göstermiştir. 1000 ppm H_2 için yanıt değeri 11,49, yanıt ve iyileşme süreleri sırasıyla 239 ve 286 saniyeydi. Gaz sensörü ölçümleri ayrıca üretilen NiO filmin p tipi iletkenliğe sahip olabileceğini de göstermiştir.

1. INTRODUCTION

The need for new energy sources that can be an alternative to fossil fuels, which have serious harm to the environment and human health and whose reserves are decreasing day by day, is increasing in parallel with the increasing population. Alternative energy sources are desired to be highly efficient, low-cost, low-waste and renewable. Solar cells and hydrogen energy are the most studied types in this context. Hydrogen, which is the combustion product of water and has a huge reserve in nature, is expected to be one of the main energy sources in the future [1]. Despite its high energy efficiency, difficulties in transporting and storing hydrogen impose limitations on the practical usability of this energy source. The fact that this gas is colorless and odorless makes it impossible to detect it with human senses. In addition, when the hydrogen concentration in the environment exceeds 4%, the possibility of high explosiveness requires very sensitive detection of this gas. For this purpose, intensive research is being carried out on various semiconductors for the detection of hydrogen gas. The most prominent of these are ZnO [2], SnO_2 [3], CuO [4], TiO_2 [5] and WO_3 [6] are semiconductors. Additionally, there are studies indicating that the NiO semiconductor, whose electrical resistance increases when exposed to any reducing gas, can be a hydrogen gas sensor [7].

NiO, which has a face-centered cubic structure, has p-type semiconductor properties because the majority of the main charge carriers consist of holes. This semiconductor has a wide band gap between 3.2 and 4 eV and good chemical stability. It is used in transistors [8], light emitting diodes [9] , photodetectors [10], electrochromic devices [11] , supercapacitors [12] and gas sensors. NiO films can be produced using techniques such as direct current sputtering (DC) or radio frequency (RF) magnetron sputtering, chemical vapor deposition, pulsed laser deposition, thermal evaporation, sol-gel, chemical bath deposition, and spray pyrolysis [13].

There are some studies in the literature where NiO thin film is used as an H_2 gas sensor. The conductivity type and electrical properties of NiO thin films produced by the PLD technique were controlled by changing the pressure of O_2 gas during the growth of the film. The response of these NiO films against H_2 was found to be 12% to 14% at operating temperatures between 80–125 °C at 30000 ppm H_2 gas concentration [14]. The reactions of NiO thin films grown by DC magnetron sputtering method to H_2 gas were investigated by coating them with Pt at 3 and 5 nm. It has been observed that platinum coated on the thin film surface increases the response to H_2 gas and platinum thickness is an important parameter. The effect of different and multi-stage annealing on the response of the NiO thin film produced by the sol-gel method to H_2 gas was investigated. It has been observed that the multistage annealed NiO thin film has higher porosity and higher gas response than other thin films. The highest gas response was found to be 68% for 3000 ppm H_2 at 175 °C [15]. The response of NiO thin films produced with the DC magnetron sputter technique at different thicknesses to H_2 was investigated. It was observed that thin films grown with 50 and 100 nm thickness gave a higher response for 500 ppm H_2 gas at 250 °C, and the 50 nm thick NiO thin film gave a higher response [16].

In this study, NiO thin film was prepared on quartz substrate using a 75W RF sputtering system. Detailed characterization of the produced films was performed by XRD, XPS, FESEM and AFM. The gas response of the produced thin film was investigated for 100 ppm, 500 ppm and 1000 ppm H_2 using a current-sensitive gas sensor measurement system.

2. MATERIAL AND METHOD

In the study, NiO thin film, whose H_2 gas response was examined, was produced by RF magnetron sputtering technique. A 99.99% pure Nickel target with a diameter of 2 inches was used to enlarge the film. While enlarging, the boiler pressure was set to 3 mTorr. Sputtering was carried out at 75 W, 300 °C substrate temperature and 45 min. The distance between the target and the substrate is set to 10 cm. Before thin film growth began, the Ni target was cleaned by sputtering with argon gas for 2 minutes. After cleaning the Ni target, growth was performed on the quartz substrate by introducing oxygen gas in addition to argon. Ag contact was deposited using Interdigitated digital electrode (IDE) on NiO thin film by physical vapor deposition (PVD) system.

The crystal structure of the films was determined by XRD measurements with Panalitical Empyrean (CuKα (λ = 1.5405 Å)). Measurements were made between angles of 10°–90°, with a step interval of 0.01°. AFM (Hitachi AFM 5100N; in tapping mode) and SEM (Zeiss Sigma 300) images were taken to investigate the surface morphology of the film XPS measurements were made with the Flex Mod Specs XPS system. Hydrogen gas sensor properties of NiO thin film were determined with a Keithley 487 picoampermeter in a current-sensitive measurement system at 300°C ambient temperature, 100 ppm, 500 ppm and 1000 ppm gas flow. In these measurements, 0.5V voltage was applied to the metal contacts on the samples.

3. RESULTS AND DISCUSSION

The X-ray diffraction spectrum of NiO thin film is shown in Figure 1. The obtained diffraction peaks correspond to angles of 36.83°, 42.79°, 62.06°, 74.33°. These angle values belong to the characteristic (101), (012), (110), (113) planes of the cubic NiO compound. The interplane distance values obtained using the well-known Bragg law were calculated as 0.24, 0.21, 0.15, 0.13 Å, respectively. These data are in accordance with JPDS card: (01-078-4383). The average lattice constant of the produced thin film was calculated as 4.226 nm, which differs from the theoretical value by 1.248. The crystallite sizes calculated using the Scherrer equation for the (101), (012), (110) and (113) directions were calculated as 11.357, 10.548, 10.277 and 9.647 nm, respectively. From XRD analyses, it can be said that there is no other formation in the structure of the NiO thin film produced and that it has a crystallization compatible with the literature.

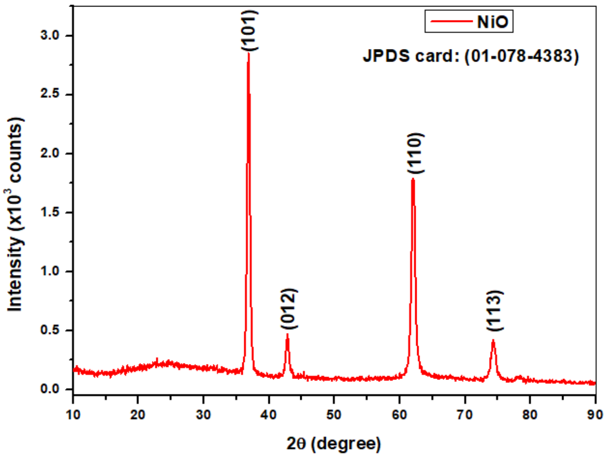

Figure 1. XRD pattern of NiO thin film.

Figure 2 shows the survey of the NiO thin film and the high-resolution XPS spectra of the O1s and Ni2p peaks. From Figure 2a, only the C1s peak is visible on the surface of the produced thin film, in addition to the characteristic peaks of nickel and oxygen This can be considered as an indication that there is no contamination other than C on the film surface. Since the binding energy of the C1s peak is 284.1 eV, a 3.3 eV shift was made in the spectrum calibration. In the O1s special scanning spectrum given in Figure 2b, two intertwined peaks are seen. After deconvolution, it can be said that these peaks correspond to the energies of 529.9 eV and 531.6 eV and belong to O^{-2} and O^{-3}. This means that there are both NiO and Ni_2O_3 structures in the structure. In the Ni2p special scan given in Figure 2c, it is seen that Ni has +2 and +3 valence, supporting the O1s spectrum. When these two spectra are evaluated together, it can be said with certainty that there is NiO and Ni_2O_3 formation on the surface.

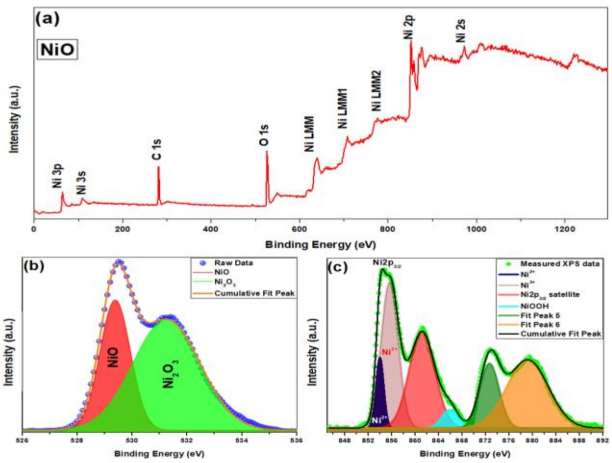

Figure 2. XPS spectra of NiO a) Survey spectrum b) High resolution O1s c) High resolution Ni2p.

SEM (Figure 3) and AFM (Figure 4) images were taken to determine the surface morphology and roughness of the NiO thin film grown by RF sputtering method. From the 20KX image given at the top of Figure 3, it can be seen that the surface is covered quite homogeneously. In the 200 KX image (Figure 3 lower part) taken for a more detailed analysis of the film surface, a lumpy structure with 1-2 nm wide gaps between them stands out. From this 20 nm scale image, it was determined that these lump-shaped structures had a size of 10-20 nm. Additionally, these images support the formation of a polycrystalline structure, as stated in XRD analyse. From the 2D AFM image obtained for a surface area of 5x5 microns (Figure 4 upper part), spherical nanostructured formations are observed on the surface of the NiO thin film. This indicates that the lumpy structures mentioned in the SEM images are spherical. Additionally, this image also indicates that the film surface has a homogeneous structure. The 3D AFM image (Figure 4 lower part) shows that the structures extending out from the surface have generally equal heights. Surface roughness values obtained from AFM analyzes were obtained as 79.61 nm for NiO film.

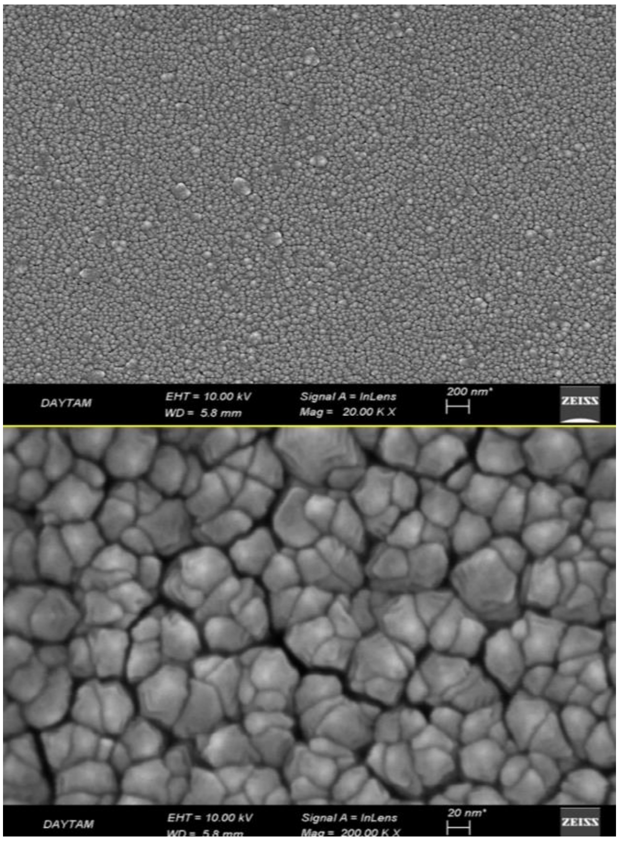

Figure 3. SEM image of NiO thin film at 20 and 200KX magnification.

The H_2 gas response of the NiO thin film obtained with the gas sensing system sensitive to current change is given in Figure 5 for different gas concentrations. In experimental measurements, H_2 gas was introduced into the environment 2 seconds after the beginning of the experiment. When 100, 500 and 1000 ppm H_2 gas was introduced, the current values measured through the sample decreased. For H_2 gas applied for 300s, current values decreased at all ppm. When the H_2 gas was cut off, the current values passing through the sample surface increased. This was repeated 3 times for each 3 different ppm values. During each cycle, the NiO thin film showed similar evolution curves upon degassing and degassing. This is a clear indication that the produced film both responds to H_2 gas and that the gas response is repeatable. The current change at 100 ppm is quite small, and the R value calculated with the formula $R=100x(I_0-I)/I_0$ was obtained as 0.08. However, it was observed that the current changes increased significantly with increasing gas concentration. R values at 500 and 1000 ppm gas values were calculated as 3.41 and 11.49, respectively. The H_2 gas response, which shows a significant increase with increasing H_2 gas concentration, indicates that the produced NiO thin film has a linear gas response. The R^2 value of the linearity graph given in Figure 6 was calculated as 0.994. In addition, at all gas concentrations, decreasing current values when gas is applied suggest that the produced film may be p-type. As a matter of fact, when p-type semiconductors are exposed to a reducing gas such as H_2, they react with oxygen adsorbed on the surface and release electrons. The resulting electrons recombine with the holes in the structure, increasing the electrical resistance of the semiconductor. This is the main reason why the current decreases when gas is applied.

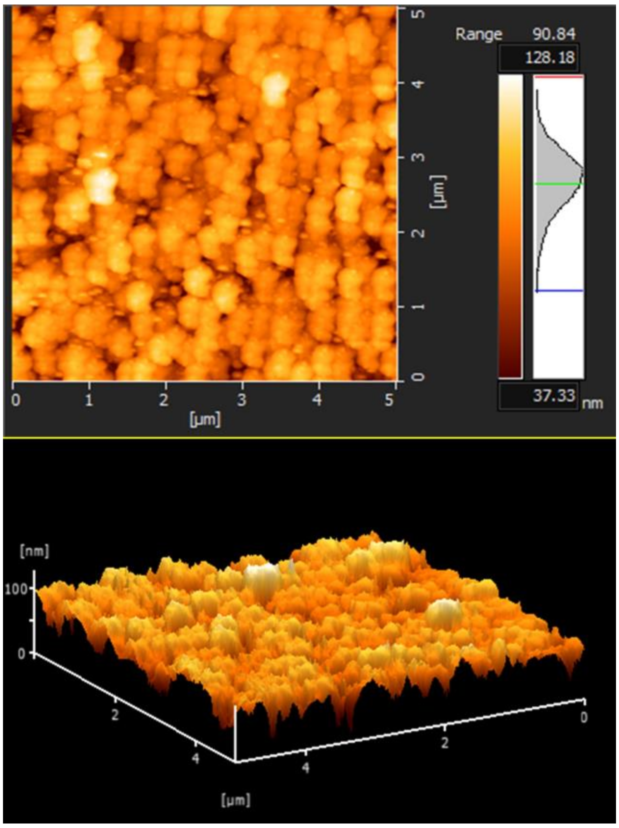

Figure 4. 2d and 3d AFM images of NiO thin film for 5x5 micron surface area.

H_2 gas response data of the produced NiO thin film at different ppm are given in Table 1. From this table, it can be seen that the response and recovery times of the film have little dependence on the gas concentration. At different gas ppm values, res and rec times are approximately 238 and 279 s, respectively. Gas response times of any material directly depend on the rate of diffusion between the gas and the element that makes up the material Since the gas responses of a single thin film at different ppm were examined in this study, there were no significant differences in the response times as expected.

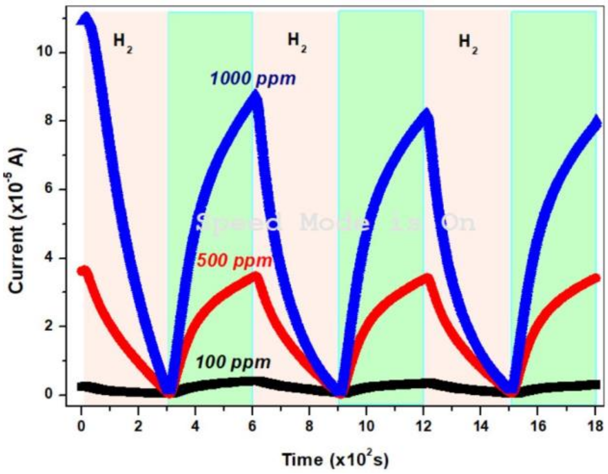

Figure 5. Current-time variation of NiO thin film for different H_2 concentrations.

Table 1. H_2 gas sensing results

H_2 concentration (ppm)	100	500	1000
τ res (s)	234	241	239
τ rec (s)	283	269	286
R	<1	3.41	11.49

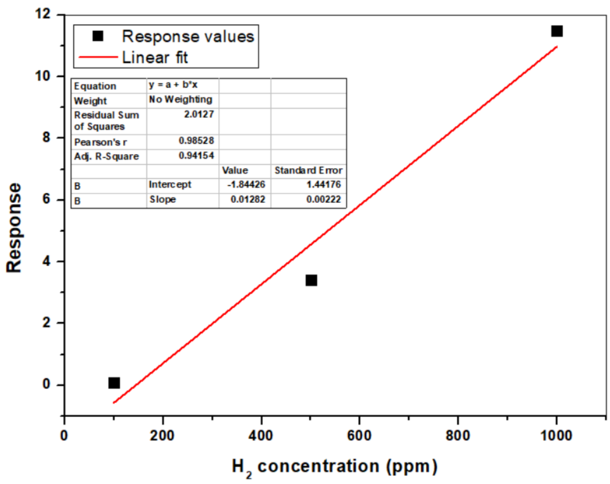

Figure 6. Linearity of NiO thin film for H_2 gas.

4. CONCLUSION

In this study, the structural and H_2 gas sensor properties of NiO thin film produced on quartz substrate by RF sputtering method were investigated. XRD measurements indicate that the structure is quite compatible with the literature and the existence of a polycrystalline cubic structure. XPS results show that NiO and Ni_2O_3 formations occur on the surface. According to the XRD and XPS results, it was revealed that no additional compounds or formations occurred in the structure, contrary to expectations. According to SEM and AFM analyses, the surface consists of very homogeneous, spherical (10—20 nm in size) nanostructures. The surface roughness value was calculated as 79.61 nm. Although H_2 gas measurements showed that the produced films had significant response values starting from 500 ppm, the response and recovery times were not significantly affected by the gas concentration. Although the H_2 gas response of the NiO film produced is lower than other studies in the literature, it is hoped that sensors with higher response values can be obtained by obtaining the p-type NiO thin film in a more porous structure. It is also predicted that surface changes can be made to obtain shorten response and recovery times.

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