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Production of high-transparent MgO films by radio-frequency sputtering method

Yüksek geçirgen MgO filmlerin radyo frekansı saçtırma yöntemiyle üretimi

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Abstract
Magnesium oxide (MgO) thin films were deposited on silicon and glass substrates by the radio frequency (RF) sputtering method. The MgO films were annealed at 400 ⁰C for 4h. The effect of working pressure on the structure and optical properties of MgO films was investigated. Structural characterization of thin films was determined using the X-ray diffraction (XRD) method. XRD results showed the presence of dominant peaks corresponding to the (200) and (220) lattice planes of MgO. However, peaks corresponding to (111), (311) and (222) lattice planes of the MgO also appeared in the films deposited at low pressure. It was determined that the average crystal size decreased as the working pressure reduced, while the deposition rate increased. SEM analysis showed that the microstructure of the nano-spherical MgO film transformed into a coarse-grained nano-pyramidal shape after annealing. The optical properties of MgO films were investigated by UV-Vis spectroscopy. Accordingly, it was determined that the absorption threshold of the films was around 310 nm wavelength and the optical band gap of the films varied between 4.07 and 4.14 eV. As a result, MgO films with high transmittance reaching an average of 95% in the visible region were obtained.

Keywords: High-transparent films, Magnesium oxide, Optical properties, RF sputtering

Öz
Magnezyum oksit (MgO) ince filmler, radyo frekansı (RF) saçtırma yöntemiyle silikon ve cam altlıklar üzerine biriktirildi. MgO filmler 400 ⁰C'de 4 saat tavlandı. MgO filmlerin yapı ve optik özellikleri üzerine çalışma basıncının etkisi araştırıldı. İnce filmlerin yapısal karakterizasyonu, X-ışını kırınımı (XRD) yöntemi kullanılarak belirlendi. XRD sonuçları, MgO'in (200) ve (220) kafes düzlemlerine karşılık gelen baskın tepe noktalarının varlığını gösterdi. Bununla birlikte, düşük basınçta biriktirilen filmlerde MgO'in (111), (311) ve (222) kafes düzlemlerine karşılık gelen pikler de ortaya çıktı. Çalışma basıncı azaldıkça ortalama kristal boyutunun azaldığı, biriktirme hızının ise arttığı belirlendi. SEM analizi, MgO filminin nano-küresel mikroyapısının, tavlamadan sonra iri taneli bir nano-piramidal şekle dönüştüğünü gösterdi. MgO filmlerinin optik özellikleri Ultraviyole-Görünür spektroskopisi ile incelendi. Buna göre filmlerin absorpsiyon eşiğinin 310 nm dalga boyu civarında olduğu ve filmlerin optik bant aralığının 4,07 ile 4,14 eV arasında değiştiği belirlendi. Sonuç olarak görünür bölgede ortalama %95'e ulaşan yüksek geçirgenliğe sahip MgO filmler elde edilmiştir.

Anahtar kelimeler: *Yüksek-geçirgen filmler, Magnezyum oksit, Optik özellikler, RF saçtırma*

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1. Introduction

1. Giriş

Magnesium oxide (MgO) is an attractive material for many applications due to its several superior properties such as high electrical resistivity, low thermal conductivity, hyper optical transparency, good chemical inertness and high secondary-electron emission (Caceres et al., 2002). MgO films have an important place especially in the field of electronics. MgO thin films are actively used as a buffer layer for the deposition of high-temperature superconductors and perovskite-type ferroelectric films (Kim et al., 2000; Lee et al., 2003). The purpose of using buffer layers in such applications is to reduce interdiffusion, lattice mismatch and other undesirable reactions (Płóciennik et al., 2016). It is also used as a protective dielectric layer to increase the lifetime of the panel in the plasma display technology (Baba et al., 2000; Eun et al., 2003). In the plasma display panel, a low discharge voltage is required to ensure high electrical efficiency. Therefore, MgO films with high secondary electron emission efficiency are used to reduce the discharge voltage in such devices. Moreover, MgO is considered as an alternative material that can be used instead of the existing dielectric material SiO_2 for capacitor applications. On the other hand, MgO thin film is mostly preferred in optoelectronic applications because of its optical properties such as wide band gap, high transparency and relatively low refractive index (Visweswaran et al., 2020). For this reason, the examination and improvement of the optical properties of transparent oxide films, which have an important position in electronic applications, will allow for the expansion of their usage area.

The MgO thin films have been produced by various mechanisms and methods such as thermal oxidation (Patil & Puri, 2011), electrochemical deposition (Chowdhury & Kumar, 2006), atomic layer deposition (Kim et al., 2013), chemical vapor deposition (Boo et al., 1999), e-beam evaporation (Cho et al., 2010), RF/DC magnetron sputtering (Eun et al., 2003; Lee et al., 2003; Nam & Han 2003), electrostatic spray deposition (Kim et al., 2000), sol-gel (Ho et al., 1997; Bazhan et al., 2013) and successive ionic layer adsorption and reaction (SILAR) (Güney & İskenderoğlu, 2018). Among all these methods, magnetron sputtering is particularly suitable for producing thin films with high homogeneity for electronic applications. The structural and optical properties of thin films can be controlled by changing sputter parameters such as power, working pressure, substrate temperature, pressure, and gaseous environment. In particular, the RF working pressure plays an important role to improve the crystallinity of MgO films. Therefore, the examination of the working pressure will a great contribution to the expansion of the usage area of MgO materials. Accordingly, in this study, high-transparent MgO thin films were grown on glass and silicon (Si) substrates by the RF magnetron sputtering method. The effect of RF working pressure on MgO thin films was characterized structurally and optically.

2. Material and method

2. Materyal ve metot

MgO thin films were deposited on Corning glass and P-type Si (100) substrates by the radio frequency (RF) sputtering system (Vaksis Handy 3M). The MgO target was used as source material for the deposition of the films. The MgO target was fabricated by pressing MgO powder (99.95% purity) into a disk (50 mm diameter × 3 mm thickness) and sintering at 1450 °C for 2h. (Kurt J. Lesker Company). MgO is a white, odorless and non-toxic material. MgO, which is a highly ionic insulating material, has a sodium chloride (NaCl) type crystal structure with face-centered-cubic (FCC). The P-type Si (100) substrates were purchased from the Maideli Advanced Materials Company Chine, whereas the Corning glass substrates were purchased from the local market. Prior to deposition, all substrates were cleaned with an ultrasonic cleaner in acetone, methanol and deionized water baths, respectively. In addition to this, the Radio Corporation of America (RCA) method consisting of two steps was used to clean the Si (100) substrates. In the first step of the RCA procedure, a solution of $NH_4OH:H_2O_2:H_2O$ was prepared by mixing at a ratio of 1:1:5, respectively. Silicon substrates were kept in this solution at 70 ºC for 10 minutes and washed with deionized (DI) water for rinsing. Then these substrates were dipped in $HF:H_2O$ (1:50) solution for 30 s and rinsed in DI water. In the second step, the Si (100) substrates were dipped into $HCl:H_2O_2:H_2O$ (mixing ratio of 1:1:6, respectively) solution at 70 °C for 10 min. Afterwards, they were etched in $HF:H_2O$ (1:50) solution for 30 s. Finally, the Si (100) substrates were rinsed in deionized water and then dried with dry nitrogen gas. The clean samples were put into the sputter system using a holder. The vacuum chamber pressure was reduced to 1×10^{-6} Torr through a turbopump. The substrate temperature was set to 300 °C and the sputter power was kept constant at 100W. The high purity (99.9%) inert argon gas was used during sputtering. The working pressures were adjusted to be 5, 7.5 and 10 mTorr for each deposition condition. Deposition parameters of MgO thin films grown by the RF sputtering method are given in Table 1. The sputtered films were annealed with a muffle furnace (Carbolite-CWF) at 400 °C for 4 h in air ambient. The annealing furnace was heated to 400 degrees with a ramp rate of 15 °C min^{-1}. After the furnace temperature stabilized, the samples were placed in the furnace and annealed for 4 hours. Then, the furnace was cooled down to room temperature slowly (~5 °C min^{-1}) to prevent crack formation.

The crystal structure of MgO thin films deposited on Si (100) substrates was characterized by the X-ray diffraction method (XRD) using a Panalytical Empyrean X-ray diffractometer with Cu Kα (λ = 1.5406 Å) radiation in a scan ranging from 30º to 90º (2θ). The thickness of the films was measured from the partially masked region using a profilometer (Kla Tencor Stylus Profiler) to determine the MgO deposition rate. The surface images of the films were examined to observe the microstructural change after annealing by scanning electron microscopy (SEM) using a Zeiss Sigma 300. The optical properties of MgO films deposited on glass substrates were determined using a UV–Vis spectrophotometer (Shimadzu UV- 600 Plus) in the wavelength range of 300–900 nm.

Table 1. Deposition parameters of MgO thin films by the RF sputtering method
Tablo 1. *MgO ince filmlerin RF saçtırma yöntemiyle biriktirme parametreleri*

Parameters	Values
Target	99.95% purity MgO, Ø50 mm, t:3 mm
Distance from substrate to target	65 mm
Substrates material	P-type Silicon (100), Corning glass
Base vacum pressure	1E-6 Torr
Flow rate of the Ar gas	50 sccm
Working pressure	5 mTorr, 7.5 mTorr and 10 mTorr
Sputtering power	100 W
Substrate temperature	300 °C
The holder rotating speed	3 rpm
Deposition time	2 h

3. Results and discussion
3. Bulgular ve tartışma

The deposition rate was determined by the ratio of the film thickness to the deposition time. The thickness of the films deposited on the Si substrate was measured using a stylus profilometer. The deposition rate of MgO thin films, which were grown at 5, 7.5 and 10 mTorr pressures for 2 hours, was calculated as 9.16, 7.52 and 5.41 Å/min, respectively. The deposition rate gradually decreased with increasing working pressure. The quantity of Ar gas in the vacuum chamber at high deposition pressures is higher than at low deposition pressure. This situation increases the collision probability of gas atoms with each other. Thus, the energy of Ar atoms bombarding the target surface is reduced, which leads to a decrease in the deposition rate. On the other hand, the mean free path is reduced by rising pressure for MgO. This causes a decrease in the energy of the sputtered atoms and an increased probability of atoms being backscattered, which is another reason for the reduction of the deposition rate.

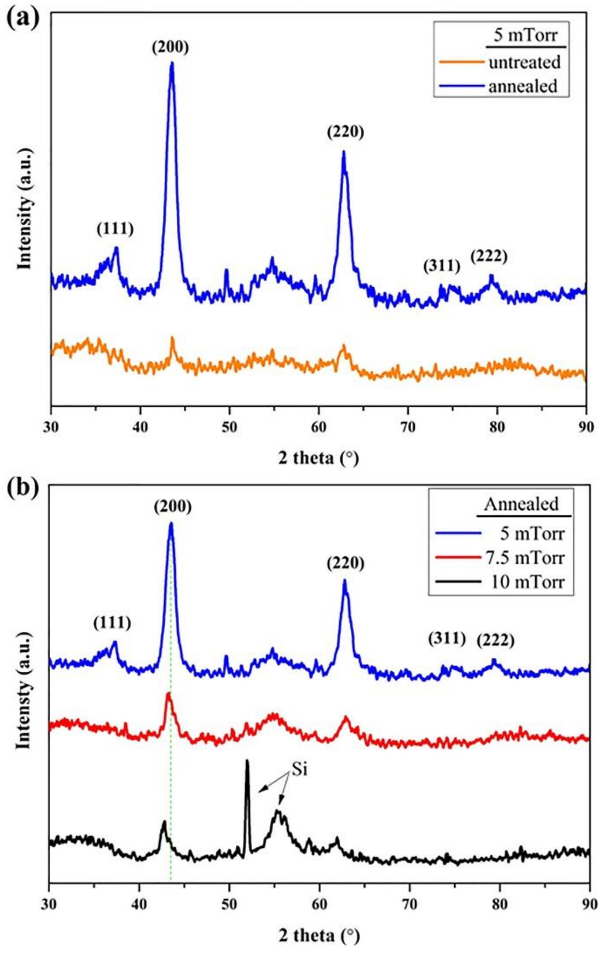

Figure 1. (a) XRD patterns of untreated and annealed MgO thin film deposited at 5 mTorr, (b) XRD patterns of annealed MgO thin films deposited at 5, 7.5 and 10 mTorr.
Şekil 1. *(a) 5 mTorr'da biriktirilen işlemsiz ve tavlanmış MgO ince filmin XRD desenleri, (b) 5, 7,5 ve 10 mTorr'da biriktirilen tavlanmış MgO ince filmlerin XRD desenleri.*

X-ray diffraction patterns of untreated and annealed MgO thin film deposited at 5 mTorr pressure are given in Figure 1(a). From this figure, it is clearly seen that the peak intensity of the thin film increased after the annealing process. In particular, the increase in the intensity of the (2 0 0) and (2 2 0) MgO diffraction peaks indicates that the annealing process considerably increased the crystallization. Figure 1(b) shows the XRD patterns of the annealed MgO thin films as a function of the working pressure. The XRD patterns revealed the presence of prominent peaks at around 2θ values of 43.5º and 62.8º corresponding to the (200) and (220) lattice planes of the MgO in all deposition conditions. However, three peaks at 2θ value of 37.4º, 73.7º and 79.2º corresponding to (111), (311) and (222) lattice planes of the MgO also appeared in low deposition conditions. Furthermore, the intensity of the diffraction peaks increased with decreasing working pressure for MgO film. This is associated with an increase in the film thickness as well as an increase in the crystallization rate of the MgO film. The average crystallite size (*D*) of MgO films corresponding to the (200) plane was calculated from the XRD data by Debye-Scherrer's equation (1) (Güney & İskenderoğlu, 2018). The average crystallite size increased from 7.12 nm to 10.78 nm with increasing working pressure, while FWHM decreased from 1.2 to 0.8. This situation demonstrated that the crystal quality of MgO film increased with increasing working pressure.

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

where λ is the X-ray wavelength (λ = 0.15406 nm), the θ is Bragg's angle, β is the half-width at half-maximum (FWHM) in radians of 2θ. Some physical parameters of MgO thin films are summarized in Table 2.

Table 2. The physical properties of MgO films grown at the different working pressure
Tablo 2. *Farklı çalışma basınçlarında büyütülen MgO filmlerin fiziksel özellikleri*

Working pressure (mTorr)	Orientation (hkl)	Degree (º)	FWHM	Average crystallite size (nm)	Deposition rate (Å /min)
5	200	43.55	1.20	7.12	9.16
7.5	200	43.30	1.16	7.33	7.52
10	200	42.75	0.80	10.78	5.41

Surface images of untreated and annealed samples were examined to observe the microstructural change after the annealing process by SEM. Figure 2 shows the untreated and annealed microstructure of MgO films grown at 5 mTorr pressure. After annealing, as seen in Figure 2(b), the fine-grained spherical structure turned into a coarse-grained pyramidal structure, which is an indication of increased crystallization. XRD data also confirmed the improvement in crystallization after annealing. This may be due to the nucleation and growth mechanism, which is more activated by annealing.

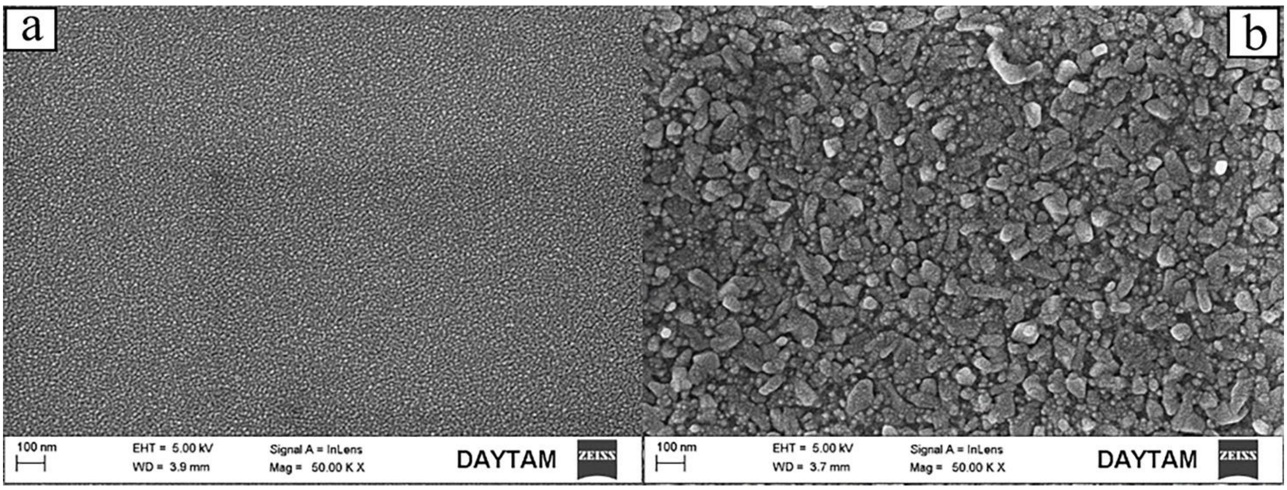

Figure 2. SEM image of the microstructure of (a) untreated and (b) annealed MgO film deposited at 5 mTorr pressure
Şekil 2. *5 mTorr basınçta biriktirilmiş (a) işlemsiz ve (b) tavlanmış MgO filmin mikroyapısının SEM görüntüsü*

The working pressure significantly affects the optical properties of the oxide films produced by the sputtering method. The optical properties of annealed MgO films deposited on glass substrates were determined using a UV–Vis spectrophotometer in the wavelength range of 300–900 nm. The absorbance spectra of annealed MgO films grown on glass substrates under different working pressures are given in Figure 3(a). It was determined that the absorbance threshold of MgO films corresponded to a wavelength of about 310 nm. The absorption edges of the films are redshifted with increasing working pressure, as seen in the detail of Figure 3(a). In addition, the highest absorption was obtained from the film grown to 7.5 mTorr pressure. Figure 3(b) shows the transmittance spectra of the films as a function of working pressure. As can be seen from this graph, it is clear that the films have very high transmittance in the visible region. The optical transmittance of the films increased from 93% to 97% at 600 nm as working pressure increased from 5mTorr to 10mTorr. The optical transmittance characteristic of materials is related to structural properties of the film such as homogeneity, crystal quality, film thickness and lattice defects such as deficiencies or vacancies (Nam & Han, 2003; Ahmed et al., 2016). In this study, the crystal quality increased with increasing working pressure and accordingly the transmittance increased. Moreover, the increase in transparency for high deposition conditions may be attributed to the decrease in film thickness, and also the decrease in native defects such as magnesium vacancies and interstitial oxygen.

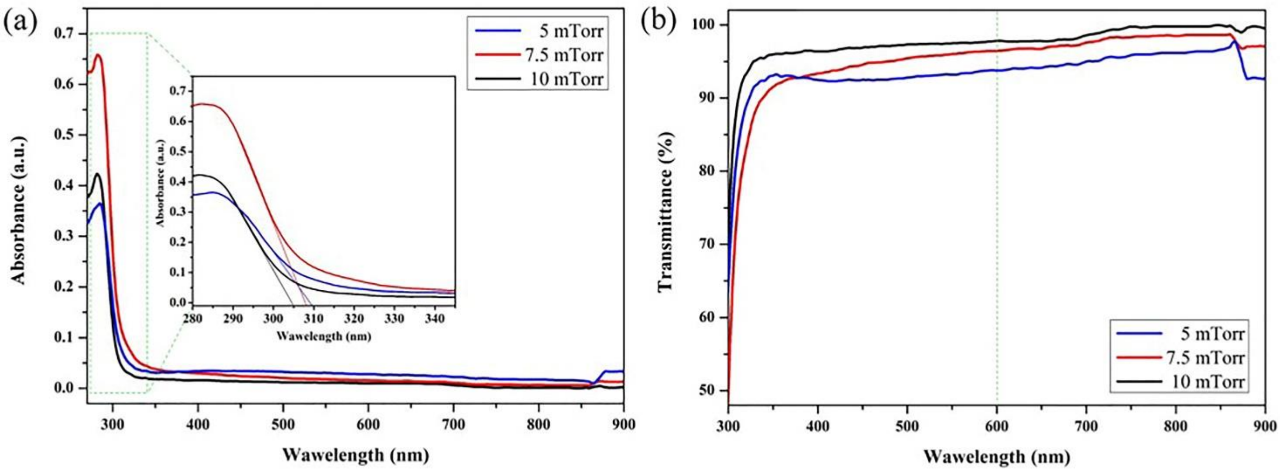

Figure 3. (a) Absorbance spectra and (b) transmittance spectra of annealed MgO films grown on glass substrates under different working pressures

Şekil 3. *Farklı çalışma basınçlarında cam substratlar üzerinde büyütülmüş, tavlanmış MgO filmlerin (a) soğurum spektrumları ve (b) geçirgenlik spektrumları*

The optical band gap plays an important role in determining the film characteristics of the material in semiconductor technology (Chowdhury & Kumar, 2006; Şenaslan et al., 2021). The optical band gap of semiconductor materials is related to the absorption coefficient (a) which is determined using the following equation (2):

$$a = \frac{Absorbance}{t} \quad (2)$$

where α is the absorption coefficient, t is film thickness. The optical band gap (allowed direct transition) of the MgO films was calculated from the absorbance data using the Tauc's equation (3):

$$ahv = A(hv - E_g)^{1/2} \quad (3)$$

where A is the band edge constant, hυ is the photon energy, E_g is the optical bandgap. Figure 4 shows the $(ahv)^2$ versus photon energy (hv) curves of MgO films as a function of working pressure. The optical band gap of the MgO films increased from 4.07 eV to 4.14 eV with increasing working pressure from 5 mTorr to 10 mTorr. The increase in band gap can be attributed to the more homogeneous structure resulting from slow growth at high working pressure. Because, as the defect level in the structure increases, the scattering effect of the light will increase, which causes a decrease in the band gap. The band gap values obtained for MgO films are consistent with the studies in the cited literature (Ahmed et al., 2016; Güney & İskenderoğlu, 2018; Visweswaran et al., 2020; Taşer et al., 2021).

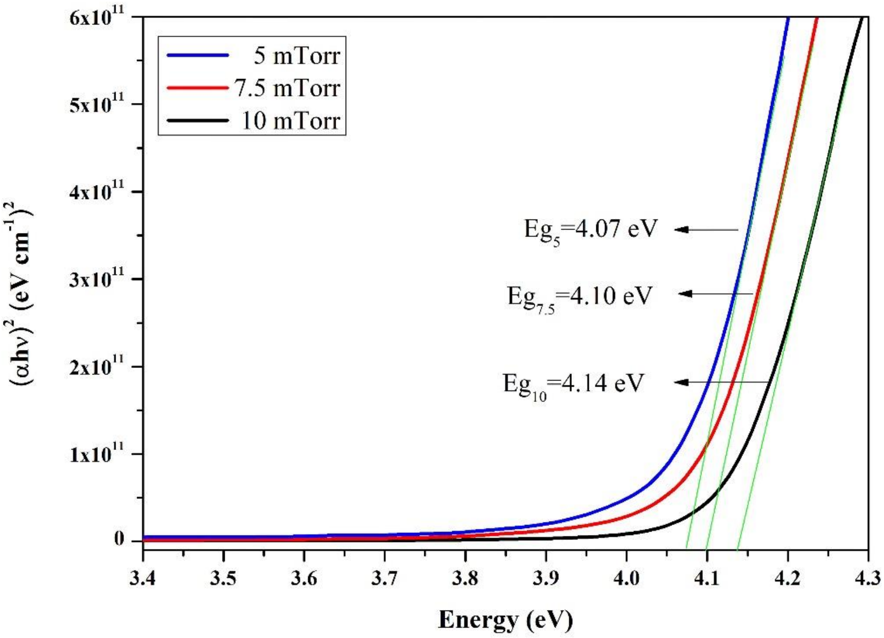

Figure 4. The bandgap energy of annealed MgO films as a function of working pressure
Şekil 4. *Çalışma basıncının bir fonksiyonu olarak tavlanmış MgO filmlerin bant aralığı enerjisi.*

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Author contribution
Yazar katkısı

Fatih ŞENASLAN: Methodology, data analysis, investigation, writing—original draft, visualization.
Ayhan ÇELİK: Conceptualization, project administration, writing—review and editing.
Muharrem TAŞDEMİR: Writing—review and editing.

Declaration of ethical code
Etik beyanı

In this study, we undertake that all the rules that must be followed within the scope of the "Higher Education Institutions Scientific Research and Publication Ethics Directive" have been complied with, and that none of the actions specified under the title of "Actions Contrary to Scientific Research and Publication Ethics" have been carried out.

The authors of this article declare that the materials and methods used in this study do not require ethical committee approval and/or legal-specific permission.

Conflicts of interest
Çıkar çatışması beyanı

The authors declare that there is no conflict of interest.

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