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Research Article

The Effects of Increasing Annealing Temperature on Some Physical Properties of a Glass/GaN/InGaN Film produced with TVA

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Abstract

In this study, GaN/InGaN semiconductor films were deposited on glass substrate using thermionic vacuum arc (TVA) method. In order to improve some physical properties of the produced films, thermal annealing was performed at different temperatures and the effect of annealing temperature on the optical and surface properties of the films was investigated. Transmittance and absorption spectra were taken using a UV-VIS spectrophotometer and optical band gap energies were determined. The surface images and surface roughness values of the films were obtained using atomic force microscopy (AFM). According to the results obtained, some physical properties of GaN/InGaN films were improved by thermal annealing and these films were investigated for use in various technological fields.

Keywords: GaN/InGaN, Transmittance, Band gap, Atomic Force Microscope (AFM), Thermionic vacuum arc (TVA), Annealing.

TVA ile üretilen Cam / GaN / InGaN Filmin Artan Tavlama Sıcaklığının Bazı Fiziksel Özelliklerine Etkileri

Öz

Bu çalışmada, GaN / InGaN yarı iletken filmler, termiyonik vakum ark (TVA) yöntemi kullanılarak cam alttaş üzerine büyütüldü. Üretilen filmlerin bazı fiziksel özelliklerini iyileştirmek için, farklı sıcaklıklarda termal tavlama yapıldı ve tavlama sıcaklığının, filmlerin optik ve yüzey özellikleri üzerindeki etkisi araştırıldı. UV-VIS spektrofotometresi kullanılarak geçirgenlik ve soğurma spektrumları alınmış ve optik enerji bant aralıkları belirlenmiştir. Filmlerin yüzey görüntüleri ve yüzey pürüzlülük değerleri, atomik kuvvet mikroskopisi (AFM) kullanılarak elde edildi. Elde edilen sonuçlara göre, GaN / InGaN filmlerin bazı fiziksel özellikleri termal tavlama ile iyileştirilmiş ve bu filmler çeşitli teknolojik alanlarda kullanım için araştırılmıştır.

Anahtar Kelimeler: GaN/InGaN, Geçirgenlik, Bant aralığı, Atomik Kuvvet Mikroskobu (AFM), Termiyonik vakum ark (TVA), Tavlama.

1. Introduction

Semiconductors constitute the basis for today's electronics technology for the reason of adjustable their energy band gaps (Pearton, 2013). Since three nitride (III-N) semiconductors have a wide band gap materials depending on their alloy densities, they can be widely used for device applications (Morkoç, 2009). GaN is a

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semiconducting compound consisting of a combination of gallium (Ga) in the column III and nitrogen (N) in the column V of the periodic table. InGaN alloy formed with GaN and InN compounds (Medjoub, 2017; Sze, 1981). Nitride based semiconductors have been used for a wide range of applications such as; light emitting diodes (LEDs), laser diodes (LDs), solar cells (Edward, 2002; Mottier, 2010). III-Nitride materials have gained an important place in modern semiconductor and electronic technology as well as modern optical devices (Ambacher, 1998; Jain et al., 2000). The design of optoelectronic and photovoltaic devices fabricated from semiconductor materials is aided by knowledge of absorption coefficient related to band gap and morphological parameteres. An accurate knowledge of band gap, and absorption measurements of semiconducting materials is very important in determining optical properties for many devices. Roughness and the band gap energy of pure and compound semiconductors are two fundamental physical quantities which characterize their surface and optical properties. Hence the possible application of semiconductors in optical and optoelectronic devices depends on knowing these characteristic values. Thermal annealing is commonly used to improve optical and superficial properties by reducing defects in materials. During the annealing process, in particular, the physical properties of the surface zone of the material may change. Many thin film coating methods such as RF sputtering Erdoğan and Kundakçı (2019a, 2019b), chemical vapor deposition Liu et al. (2017), Yang et al. (2008) pulsed laser deposition Li et al. (2015), Shen et al. (2012) are used when preparing GaN/InGaN thin films. One of these methods, thermionic vacuum arc (TVA), is a useful method for preparing nitrides coatings because of its ability to be controlled under each phase, simple devices required, and low temperature applications. Recently, InGaN thin films on ITO substrate have been deposited and investigated by our group (Erdoğan and Kundakçı, 2019c). Different substrate such as polyethylene terephthalate (PET) was used to GaN growth on it with the TVA method (Pat et al., 2015). A few experimantal studies have been reported about thermal annealing process of GaN and InGaN thin films in the literature. Wickenden et al. (1994) investigated only the structural characterization of the GaN nucleation layers on sapphire susbtrate. They reported that, when the films heated to higher temperatures, the crystal size grows and the crystal evolves significantly to near the optimum single crystal material until it is empirically close to optimum temperatures for growth of an epitaxial upper layer. Feng et al. (2004) studied on thermal annealing effects on the size and composition variations of indium deposited clusters in two InGaN thin films with photoluminescence (PL) in yellow and red gaps and variations on post-growth thermal annealing of optical measurements and material analyzes. Feng et al. (2003) have investigated in the optical and material properties of an InGaN thin films with the average indium contents at 0.31 comparing as-grown and post-growth thermally annealed conditions with cathodoluminescence (CL) spectra in their different study. Chaudhari et al. (2011) investigated the structural and electrical properties of GaN thin films gowrn on Si(100) substrate by electron beam evaporation method. They reported that XRD and SEM of (100) GaN / Si show that the crystallinity of films with is increased a temperature of 600°C. The C-V measurement of GaN thin films precipitated on Si (100) annealed at 600°C shows the high frequency distribution in the deposition region. Thaler et al. (2010) studied the thermal stability of 200 nm thick InGaN thin films on GaN was investigated using isothermal and simultaneous post growth annealing. $In_xGa_{1-x}N$ films (x = 0.08-0.18) were annealed at 600-1000°C in N_2 for 15-60 minutes and monitored X-ray diffraction (XRD) and photoluminescence (PL) measurements. Wang et al. (2013) studied InGaN films with indium contents of 33% and 60% were precipitated by pulsed laser deposition (PLD) at a low growth temperature of 300°C. The films were then annealed at 500-800°C for 15 minutes by addition of N_2 atmosphere. They reported the effect of annealing temperature on crystal structure, indium content and InGaN emission characterization. Kazaziz et al. (2016) investigated the effects of Rapid Thermal Annealing (RTA) on the structural, electrical and optical properties of polycrystalline InGaN thin films deposited by molecular beam deposition on amorphous silicon plates. In that paper, the structural, electrical and brightness properties of the films were evaluated using X-ray diffraction (XRD), Hall effect and photoluminescence (PL) measurements, respectively. The optical properties of the films were examined in detail using variable angle spectroscopic ellipsometry (VASE). As can be seen from the work done, the effect of the structural and optical properties depends mainly on the annealing temperature. This study presents a different contribution to the literature due to the use of TVA as a different technique and the fact that the annealing effect is based on optical and superficial properties. In addition, the GaN/InGaN heterojunction structure was used as a film different from the literature. Our aim in this study is investigation of the effect of thermal annealing on optical and surface properties of glass/GaN/InGaN thin film structure produced by TVA technique. The determination of the optical constants and surface parameters as a function of temperature is expected to extend the available physical information.

2. Material and Methods

GaN/InGaN thin film has been deposited on a glass substrate using TVA, a plasma deposition technique, with very short production time being 40 s (Özen et al., 2016). An InGaN film is lying on the top of a GaN one. There are two discrete films in the structure studied. In the growth system, GaN and In metal basis powders has been puschased and they were used as pellets. Firstly, GaN was put on the growth system, and then In was put on the system. This method basically operates according to the principle of producing the plasma of the material to be formed thin film and coating the produced plasma on a desired material. A direct heated cathode is an electron gun that provides electron emission by passing current through it. Anode material crucible is made of materials with high melting temperatures. The film was deposited at 10^{-6} torr working pressure, 18 A filament current. Plasma was produced at 200 V, 0.6 A plasma current at room temperature. GaN compound and elemental In metal basis were put in the crucible as source materials. Annealing process is a preferred method for many different purposes scuh as, improving the mechanical properties of metals, to crystallizing a semiconducting material. Rapid Thermal Processing (RTP) can be used to heat the materials at high temperatures in a vacuum environment or under the desired gas in a sensitive and rapid manner and to slow down or cool rapidly according to the desired conditions. The obtained films were annealed with RTP at different temperatures (100-

400°C) for 2 minutes at N_2 environment. The thickness of deposited InGaN film was measured using an interferometer and the thickness measurement system Filmetrics F20. The average thickness of the thin film was found to be about 250 nm. The optical properties of the films have been studied via absorption measurements with ultraviolet–visible spectroscopy (UV/VIS) in the wavelength range of 200–800 nm. Surface morphology properties of the glass/GaN/InGaN film structure were investigated by a Hitachi AFM 5000 II device.

3. Resarch Findings

In this study, the effects of thermal annealing on optical and surface properties of Glass/GaN/InGaN thin film structure produced by thermionic vacuum arc technique were investigated. Structural, chemical microanalysis and electron microscopy properties of as-deposited films have been already published elsewehre (Erdoğan et al., 2016). This section has been occurred in two stages. In the first stage, optical analysis of the films such as, absorbance, transmittance, first derivative of the transmittance and optical band gap were investigated. In the last stage, surface analysis of the films such as, two and three dimensional 2x2 micron surface images and rougness parameters were investigated.

4. Results

The absorption spectra of glass/GaN/InGaN thin film structure are given in Fig. 1. From the absorbance spectra, it is noted that all films behave as opaque materials due to their high absorption properties in short wave lengths. The absorbance values of the films are sharply increased due to the increased of absorption properties of the films at wavelengths shorter than about 325 nm. These regions where the sharp increase is observed in absorbance values are the basic absorption regions of the films. In addition, as seen in Fig. 1, the magnitude of the absorbance of the film at 400°C annealing temperature is higher than that of the annealed and as-deposited films. The absorbance of the glass/GaN/InGaN system increases with annealing temperature.

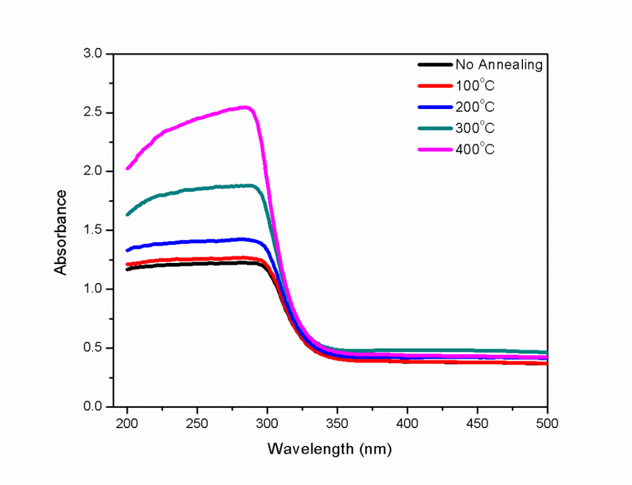

Figure 1. The plot of the absorbance vs. wavelength of the glass/GaN/InGaN thin film structure as a function of temperature

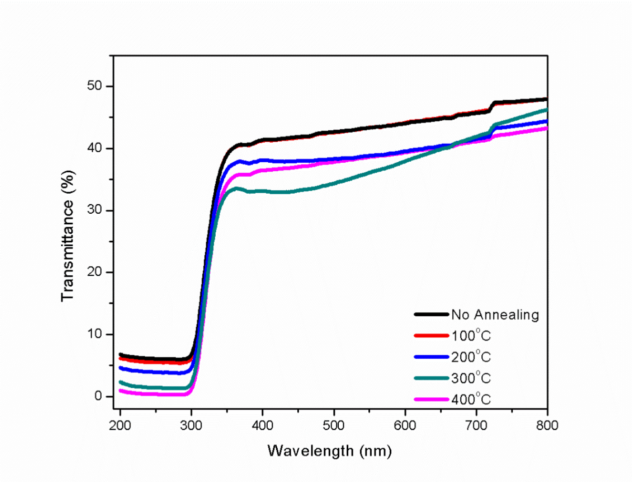

Figure 2. The plot of the transmittance vs. wavelength of the glass/GaN/InGaN thin film structure as a function of temperature

The transmittance spectra of the film are shown in Fig. 2. When the transmittance spectra are examined, it was determined that the transmittance of the films decreased with the effect of the annealing and the edge of the band deteriorated. We think that the decrease in the transmittance values can be due to the effect of annealing and the reflection losses due to the increase of the smoothness of the film surfaces. This result is supported by the reduction of surface roughness values of films (Table 2). As seen in Fig. 2, the transmittance spectra of the film show a sharp absorption edge in the range of 287–369 nm at as-deposited and 100°C, 282–367 nm at 200°C and 400°C, and 288-363 nm at 300°C. In the visible region, the average transmittance values of structure were found to be 44.0, 44.0, 39.8, 37.8 and 39.2 % from as-deposited to 400°C annealing, respectively. To estimate the absorption band edge of the films, the first derivative of the optical transmittance can be computed. The curves of dT/dλ versus wavelength were plotted, as shown in Fig. 3.

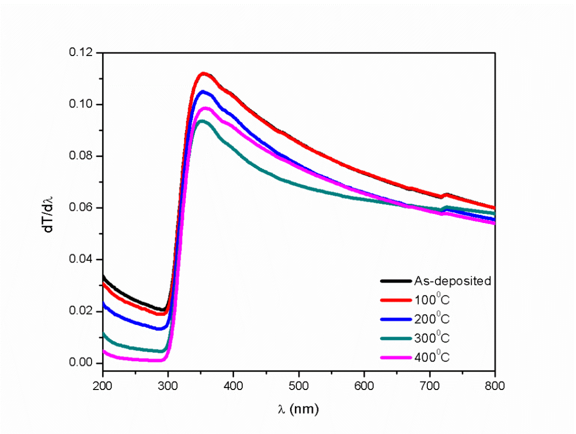

Figure 3. Plot of the first derivative of the transmittance spectra of the glass/GaN/InGaN thin film structure as a function temperature.

As seen in Fig. 3, the maximum peak position corresponds to the absorption band edge. The maximum peak values of the films were found to be 355, 355, 353, 352 and 357 nm from as-deposited to 400^{0}C annealing, respectively. Thus, the absorption band edge values of the structure were found to be 3.36, 3.36, 3.38, 3.41 and 3.38 eV from as-deposited to 400^{0}C annealing, respectively. The absorption band edge values of the film increase with annealing temperature until 400^{0}C annealing temperature. At that temparature, absorption band edge value decreases. In the near ultraviolet and visible region, the average transmittance (T_{avg}) values of the glass/GaN/InGaN thin film structure as a function of annealing temperature were calculated and given in Table 1.

Table 1. The T_{avg} -NU (in the near ultraviolet region), T_{avg} -V (in the visible region), $\lambda_{max\text{-}peak}$, absorption band edge (abe), Eg, λ_{Tfd} (wavelengths at first decrease of transmittance) and E_{Tfd} values of the glass/GaN/InGaN thin film structure

	$T_{avg\text{-}NU}$ (%)	$T_{avg\text{-}V}$ (%)	$\lambda_{max\text{-}peak}$ (nm)	abe (eV)	E_g (eV)	λ_{Tfd} (nm)	E_{Tfd} (eV)
As-depostied	17.0	44.0	369	3.36	3.39	355	3.49
100°C	16.6	44.0	369	3.36	3.37	355	3.49
200°C	14.7	39.9	367	3.38	3.35	353	3.51
300°C	11.8	37.8	363	3.41	3.46	352	3.52
400°C	11.6	39.2	367	3.38	3.53	357	3.47

The optical method is used to determine the optical energy gaps of the film. Using the absorbance spectra of the film, the linear absorption coefficient of the film is calculated from the expression (Chambouleyron and Martinez, 2002):

$$\alpha = \frac{1}{d}[2.3 * A + ln(1-R)^2] \quad (1)$$

where d is thickness of the film, A is the absorbance value and R is the reflectance value. To determine the energy band gap values, we plotted $(\alpha hw)^{1/2}$ versus (hw) where α is the absorption coefficient and hw is the photon energy. The absorption coefficient α is proportional to (Tauc and Menth, 1972; Stenzel, 2005):

$$\alpha(hw)=B(hw-Eg)^{n} \quad (2)$$

where B is a constant, Eg is the optical band gap and n assumes values of 1/2, 2, 3/2, 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. This graph $[(\alpha)^{1/2}$ versus $(hw)]$ has given as a function of temperature in Figure 3. The band gap energy of thin film has been then determined by the extrapolation of the linear region on energy axis as shown in Fig. 4.

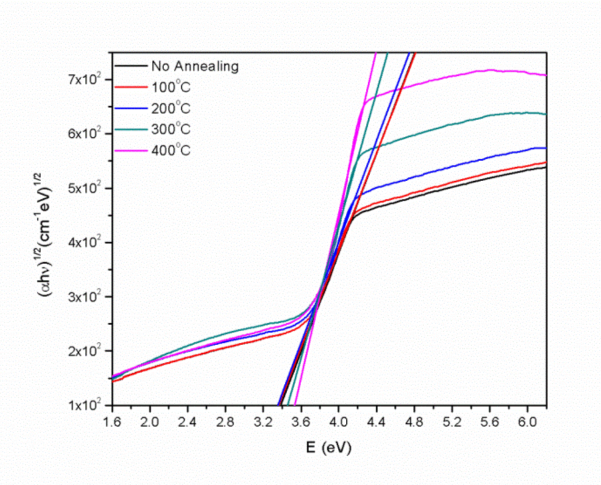

Figure 4. The $(\alpha h\nu)^{1/2}$ plot vs. the photon energy (E) of the glass/GaN/InGaN thin film structure as a function of temperature

Obtained graphs show that the optical energy gaps are changed to 3.39, 3.37, 3.35, 3.46 and 3.53 eV, and are suitable for solar cell applications. In addition, it has been observed that films with annealing temperature decrease in optical energy gaps until the annealing temperature of 300°C, then increase again. We think that the drop and icrement in band gap values may be due to band dangles caused by deformation in the structure due to the deviations in the stoichiometry. Distortion at the band edges is also evident from the transmittance and absorption spectra. The obvious change in the optical properties of films with annealing is a classically expected change. The logic here is based on the principle that the atoms in the film go to where they should have been by heating because of the thermodynamically unstable construction of the structure. It is also generally known that other defects in solids are corrected by annealing such as radiation-induced disorder, surface energy states, cavities. In our examples, although the expected annealing effect is observed, the effects that compete with it and distort the films are also observed. The decrease in optical band gap energy is seen in the heated direct-transition-type semiconducting thin films. It has been observed that an optical band gap shift of ZnO thin films was from 3.31–3.26 eV after annealing (Kang et al., 2004).

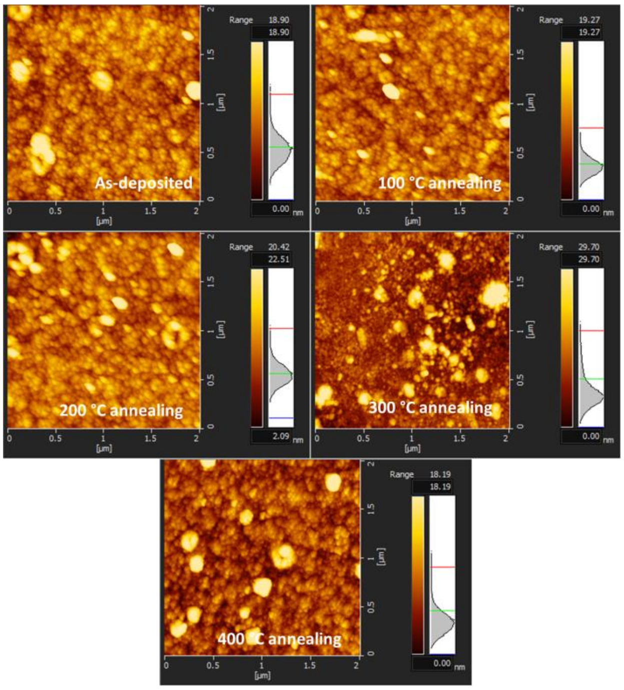

Figure 5. Two (2D)-dimensional 2 x 2 μm^2 scan area topography images of AFM of the glass/GaN/InGaN thin film structure as a function of temperature

Surface morphology properties of the glass/GaN/InGaN film structure as a function of annealing temperature were investigated by an Atomic Force Microscopy (AFM) (Raposo et al., 2007). Two and three dimensional 2x2 micron surface images obtained by atomic force microscopy of the films are given in Fig. 5 and Fig. 6, respectively. When these images are examined, it can be said that the surface structure in all films is island type growth.

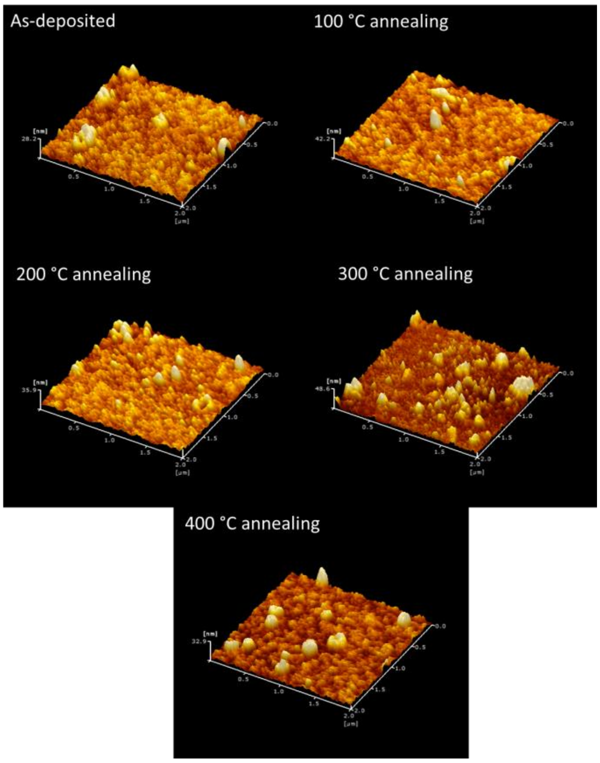

Fig.6. Three (3D)-dimensional 2 x 2 μm^2 scan area topography image of AFM of the glass/GaN/InGaN thin film structure

It is noteworthy that in all films, some regions are stacked at different heights and sizes. We think that for stacking in different regions during film formation may be the thermal properties of the glass bases used and the thermal differences between the base and the film. Additionally, it is more likely to be the result of the fast deposition technique, potential splattering of the source material, and the low surface mobility of atoms on the surface. Table 2 gives the surface roughness values of the films. It is noteworthy that the surface roughness of the films decreased with the effect of the annealing. This is an indication of the smoothness of the film surfaces.

Table.2. Surface roughness parameters of glass/GaN/InGaN thin film structure as a function of temperature

	Glass/GaN/InGaN				
(in nm size)	As Deposited	100 ^{0}C	200 ^{0}C	300 ^{0}C	400 ^{0}C
Roughness average (Ra)	3.08	2.85	2.23	1.63	1.37
Surface roughness (Rq)	4.34	3.86	2.84	1.93	1.64
Peak (Rp)	8.64	4.20	4.27	1.69	1.31
Valley (Rv)	5.50	4.18	3.89	6.29	5.65
Peak-Valley (Rt)	14.14	8.38	8.16	7.98	6.96

In this study, the effects of thermal annealing on optical and surface properties of glass/GaN/InGaN thin film structure produced by TVA method were investigated. Since GaN and InGaN films are materials that have the potential to be used in thin film solar cells, laser diodes, it is very important that they can be produced at low cost. Therefore, in this work, TVA method is used which is useful for producing these films at low cost, in high purity, and fast production time. As a result of the annealing process, it was determined that the transmittance of the films decreased with the effect of the annealing and the edge of the band deteriorated and the absorption band edge values of the film increase with annealing temperature until 400°C annealing temperature. At that temparature, absorption band edge value decreases. It has been also observed that films with annealing temperature decrease in optical energy gaps until the annealing temperature of 300°C, then increase again. Surface images of GaN/InGaN films were investigated using atomic force microscopy. It was found that the effect of the annealing process decreased the surface roughness of the GaN/InGaN films and the smoothness of the surfaces accordingly. As a result, it has been determined that the optical and surface properties of GaN/InGaN films change depending on the thermal annealing.

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