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Structural and Optical Properties of Zinc Nitride Films Prepared by Pulsed Filtered Cathodic Vacuum Arc Deposition *

ŞENADIM TÜZEMEN Ebru[1**], KAVAK Hamide[2], ESEN Ramazan[2]
[1]*Department of Physics, Cumhuriyet University, 58140 Sivas, Turkey*
[2]*Department of Physics, Çukurova University, 01330 Adana, Turkey*

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Polycrystalline zinc nitride films are deposited on Corning 7059 glass substrates by pulsed filtered cathodic vacuum arc deposition (PFCVAD). The crystallographic structure is studied by means of x-ray diffraction. These measurements show that all the films are crystallized in the cubic structure, in a preferred orientation along the (332) and (631) directions. Weak XRD signal shows small crystallites distributed in an amorphous tissue. A small improvement of crystallinity is observed with annealing. Optical parameters such as absorption, energy band gap, Urbach tail, extinction coefficients have been determined. The Urbach tail energy is decreased with annealing at 500°C for one hour. Energy band gap values are found to be increased by annealing.

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Nitride semiconductors are an inorganic semiconductor compound which have high band gap energy, electron saturation velocity and breakdown voltage.

The crystalline structure of Zn_3N_2 was resolved in the year of 1940 as a cubic *anti*-bixbyite structure.[1] Kuriyama *et al.*[2] synthesized zinc nitride onto quartz substrates and found a cubic structure with lattice constant $a = 0.978(1)$ nm. Zinc nitride has an energy band gap value about 3.2 eV. This material can be regarded as a wide band gap semiconductor. The energy band gap of zinc oxide is known to be in the vicinity of this value (3.3 eV).[3−5] The crystalline structure was clarified by Partin *et al.*[6] in 1997. Futsuhara *et al.*[7] worked on zinc oxynitride ($Zn_xO_yN_z$) compound deposited on glass substrates. They found that optical energy band gap values decrease from 3.26 to 2.30 eV with the increase of nitrogen concentration in the films. The electrical and optical properties of the zinc nitride films deposited on the borosilicate glass were investigated by Futsuhara *et al.*[8] They found direct energy band gap to be 1.23 eV. Zong *et al.*[9] found a different energy band gap to be 2.12(3) eV and an optical transition is found to be of indirect type. Orientation of the films were in the directions of (321) and (442) with a lattice constant of $a = 0.979(1)$ nm. Zinc nitride empty balls were synthesized in the year 2006.[10] The lattice constant was found to be $a = 0.9788$ nm.

Many deposition techniques were employed to produce zinc nitride films such as rf magnetron sputtering[9] and molten salt electrochemical process.[11] In this work we report the properties of the films obtained by a pulsed filtered cathodic vacuum arc deposition (PFCVAD) technique. The pulsed cathodic vacuum arc deposition technique is a new way to produce good quality (harder, denser and cleaner) thin films and coatings at low temperatures. The near 100% ionization of the cathode materials in the plasma means that the impact energy of the depositing ions at the growth surface can be readily controlled using electric fields. Their high energy plasma plume will readily ionize most background gases. These features make the pulsed cathodic vacuum arc an ideal source for the production of metal oxides and nitrides. In addition, the pulsed filtered cathodic vacuum arc deposition technique is able to control the thickness at the atomic scale and there is no need to cool the system.

Thermal annealing is a method widely used to improve crystal quality and to study structural defects in materials. The structural and optical properties are crucial for semiconductor devices especially for light emitting devices. It is necessary to study how the properties are affected by thermal annealing. Thermal annealing is also used to activate dopants in semiconductors.

The details of the PFCVAD system have been described elsewhere.[12] The cylindrical vacuum chamber was made of stainless steel (486 mm diameter and 385 mm in length) and evacuated using a primary and a turbo molecular pump (500 L/s) to a base pressure below 1.3×10^{-8} Torr. In this system, a metallic zinc (2 mm in diameter and purity 99.99%) which was held in an alumina ceramic tube was employed as cathode target, and nitrogen (purity 99.9999%) was employed as the reactive gas. Films were deposited on ultrasonically cleaned glass substrates which were located 19 mm away from the anode. Nitrogen gas was input into the chamber directly by a mass flow controller with constant flow rate.

In this study, deposition parameters for zinc nitride thin film were as follows: nitrogen pressure dur-

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** To whom correspondence should be addressed. Email: esenadim@cumhuriyet.edu.tr or Ebru_Senadim@hotmail.com ing the deposition 3×10^{-4} Torr in fixed arc current of 650 A. The distance from the target to the substrate was maintained to be 19 mm. Deposition thickness pattern of the system was determined and the substrate was placed to the most homogeneous zone.

X-ray diffraction technique was used to specify the structural parameters, the existent phases and the orientation of zinc nitride thin films. The x-ray diffraction measurements were performed by using a Rigaku Rint-2200 x-ray diffraction system equipped with Cu K_α radiation of average wavelength 1.54059 Å.

The optical properties of zinc nitride thin films deposited by PFCVAD were measured by a double beam computer controlled spectrophotometer (Perkin Elmer Lambda 2S) in the UV/VIS/NIR regions. The optical transmittance and absorbance at normal incidence were recorded in the wavelength range of 190–1100 nm and with 1 nm precision. A Filmetric model F30 was employed to measure the thickness of the zinc nitride thin film. The F30 is a spectral reflectance system that measures the thickness and optical constants of translucent thin film layers on opaque and transparent substrates.

Zinc nitride is a semiconductor with the cubic *anti-bixbyite* structure (anti-Mn_2O_3 type, Fig. 1).[11]

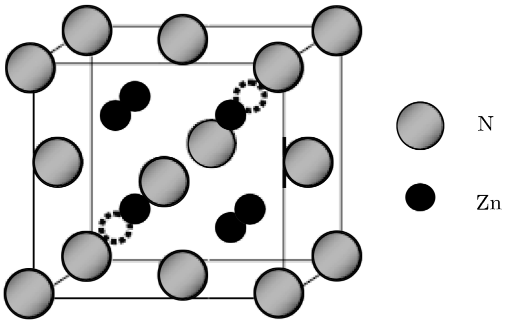

Fig. 1. Crystal structure of Zn_3N_2.

The crystalline quality and orientation of the zinc nitride films have been investigated by means of x-ray diffraction (XRD). Figure 2 shows the x-ray diffraction patterns of the zinc nitride (332) and (631) peaks of the films, as-deposited and after annealing 1 h at 500°C. The bottommost graph belongs to the as-grown zinc nitride sample and this is followed by that obtained after annealing at 500°C for 1 h. As seen from Fig. 2, the intensity of (332) peak increases as the intensity of (631) peak decreases at 500°C annealing temperature. In addition, diffraction angle (2θ) has moved to the lower values. The full width at half maximum (FWHM), interplanar distance d, lattice constant a are increased after annealing at 500°C for one hour. The results are given in Table 1. The XRD peak values are small when compared with the published data.[1,2,9] This suggests that our samples show islands connected by an amorphous zinc nitride tissue. The annealing process lowers the substrate-film stress value and lattice constant shifts to the higher values. Moreover, since the XRD signal is very strong, the lattice constant obtained from (332) peak should be taken with precaution. The (631) diffraction peak gives the lattice constant value similar to the published data.[1,2,9]

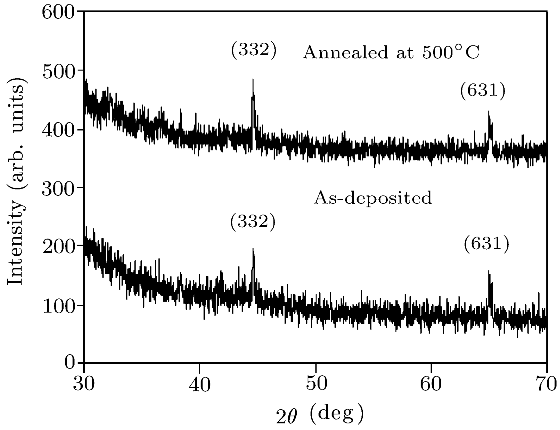

Fig. 2. XRD patterns of as-deposited and annealed zinc nitride films on Corning 7059 glass substrates.

Table 1. X-ray diffraction data of as-deposited and annealed zinc nitride films grown by pulsed filtered cathodic vacuum arc deposition on Corning 7059 glass substrates.

	Angle (2θ)	FWHM (deg)	Assignments	d (Å)	a (Å)
As-deposited	44.635	0.215	332	2.0285	9.514
	65.019	0.208	631	1.4333	9.721
Annealing at 500°C	44.621	0.256	332	2.0291	9.517
	65.004	0.220	631	1.4336	9.723

The optical transmittance spectra of pulsed filtered cathodic vacuum arc deposition zinc nitride films on a Corning 7059 glass substrate were measured with a double-beam spectrometer. From the interference fringes, the thickness d of the film was calculated by using the relation

$$d=\frac{\lambda_1\lambda_2}{2n(\lambda_2-\lambda_1)}, \tag{1}$$

where n is the refractive index, λ_1 and λ_2 are the wavelengths of adjacent peaks in the transmittance spectrum. Also, a Filmetric model F30 was employed to measure the thickness of the zinc nitride thin film. For $n=2.0$,[9] we can have the film thickness $d=161$ nm.

Figure 3 illustrates the optical transmittance spectra of a 161-nm-thick zinc nitride film deposited on a Corning 7059 glass substrate for the as-deposited and annealed in air for one hour at 500°C. The optical transmittance spectra of the sample were recorded before and after the annealing process. The average transmittance of the films in the visible range is over 90%. With annealing, the transmittance of the film is decreased due to the annealing effect. As is seen from Fig. 4, annealing has a dramatic improvement effect on the optical properties of zinc nitride. The annealed film exhibits a sharper band edge structure in the vicinity of 3 eV. Our zinc nitride films show an increase of about 1 eV in optical energy gap extrapolation. It is interesting that the above-mentioned improvement of the optical properties does not show a parallel improvement of crystalline structure (i.e. XRD peak data do not change significantly).

The absorption coefficient α is calculated by

$$T = (1 - R)^2 \exp(-\alpha d), \tag{2}$$

where T is the transmittance, R is the reflectance, and d is the thickness of the film. Since the reflectivity is negligible and insignificant near the absorption edge, this relation reduces to

$$\alpha = \frac{2.3A}{d}, \tag{3}$$

where A represents the absorbance.

The photon energy dependences of the absorption coefficients of the zinc nitride films for the as-deposited and annealed for one hour in air at 500°C are shown in Fig. 4. Band edges values for the as-deposited and annealed sample at 500°C are determined to be 2.47 eV and 3.204 eV, respectively, using the data shown in Fig. 3.

To determine the band gap E_g, we have used the plot of Tauc *et al.* in Ref. [13], where the absorption coefficient α is a parabolic function of the incident energy and optical band gap E_g is given by

$$\alpha = A(h\nu - E_g)^{1/2}/h\nu, \tag{4}$$

$$\alpha = A'(h\nu - E_g)^2/h\nu, \tag{5}$$

where A and A' are functions of refractive index of the material, reduced mass and speed of light. The above relationships are valid both for the direct transition approach equation (4) and for the indirect transition approach equation (5). The plots of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ as a function of the energy of incident radiation are shown in Fig. 5 and Fig. 6. The energy band gap can be evaluated from the intercept of the extrapolated linear part of the curve with the energy axis. The optical energy band gap of the films for direct transition increases from 2.91 eV to 3.24 eV with annealing. The optical energy band gap of the films for indirect transition increases from 1.91 eV to 3.06 eV with annealing

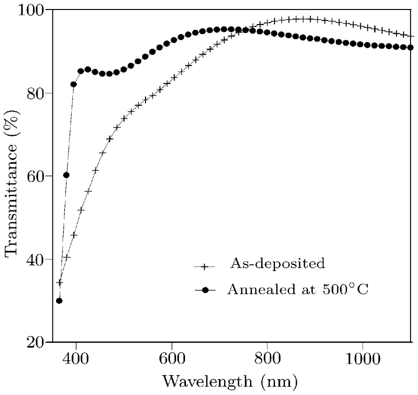

Fig. 3. Transmittance spectra of as-deposited and annealed zinc nitride films on Corning 7059 glass substrates.

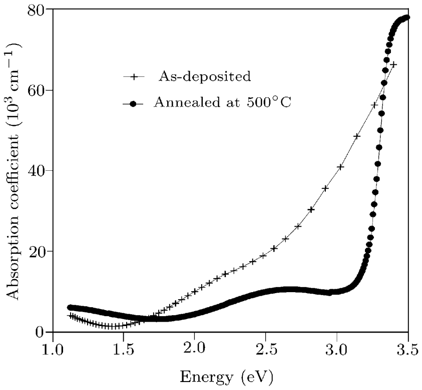

Fig. 4. Absorption coefficient of as-deposited and annealed zinc nitride films on Corning 7059 glass substrates.

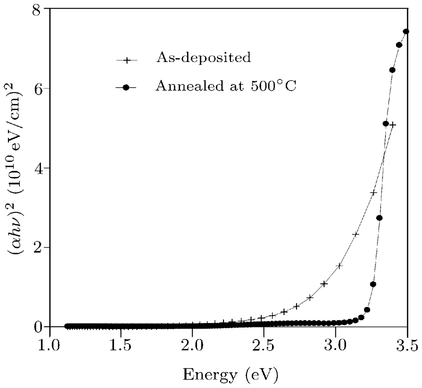

Fig. 5. Variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ of as-deposited and annealed zinc nitride films on Corning 7059 glass substrates for direct transition.

The variation of extinction coefficient is defined by

$$k = \frac{\alpha\lambda}{4\pi}. \tag{6}$$

The extinction coefficient k as a function of wavelength of the films is shown in Fig. 7. In this figure, the extinction coefficient as a function of wavelength decreases from 0.143 and 0.034 to 0.012 and 0.022, respectively, for the films as-deposited and annealed at 500°C. The decrease of the extinction coefficient with the increase of annealing can be related to the change in the transmittance of the films.

According to the result of Tauc *et al.*,[13] it is possible to separate three distinct regions in the absorption edge spectrum of amorphous semiconductors. The first is the weak absorption tail, which originates from defects and impurities, the second is the exponential edge region, which is strongly related to the structural randomness of the system and the third is the high absorption region that determines the optical energy gap. In the exponent edge where the absorption coefficient, α lies in the absorption region of $1 < \alpha < 10^4\,\mathrm{cm}^{-1}$, and the absorption coefficient is governed by the relation[14]

$$\alpha = AE_0^{3/2} \exp(h\nu/E_0) \quad \text{for} \quad h\nu < E_g, \tag{7}$$

where E_0 is an empirical parameter describing the width of the localized states in the band gap due to the above-mentioned effects. Figure 8 illustrates the semi-logarithmic plot of α as a function of E in the photon energy region where $\alpha < 10^4\,\mathrm{cm}^{-1}$. The value of E_0 is calculated from the slope of the linear plot illustrated in Fig. 8. From this figure it is clear that defects decrease with annealing. E_0 is found to be 0.74 eV for the as-deposited zinc nitride film and to be 0.14 eV for the zinc nitride film annealed at 500°C. E_0 characterizes the slope of the exponential-edge region and the inverse of slope gives the width of the localized states associated with the amorphous state in the band gap of the thin film. Urbach's absorption edge is formed in the region of photon energies below the forbidden band gap. The interaction between lattice vibrations and localized states in the tail of the band gap of the compound has a significant effect on the optical properties of the thin film.

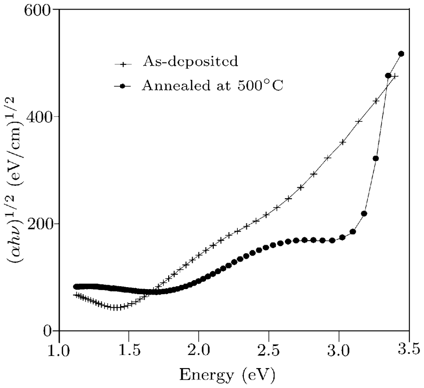

Fig. 6. Variation of $(\alpha h\nu)^2$ with photon energy $h\nu$ of as-deposited and annealed zinc nitride films on Corning 7059 glass substrates for indirect transition.

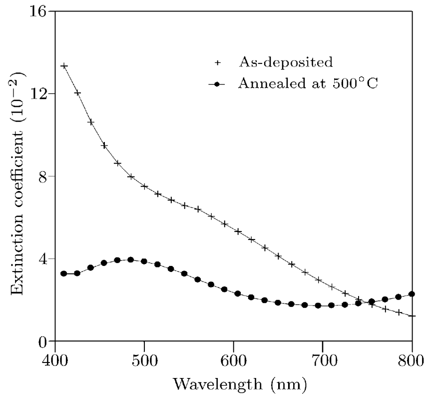

Fig. 7. Extinction coefficient of as-deposited and annealed zinc nitride films on Corning 7059 glass substrates.

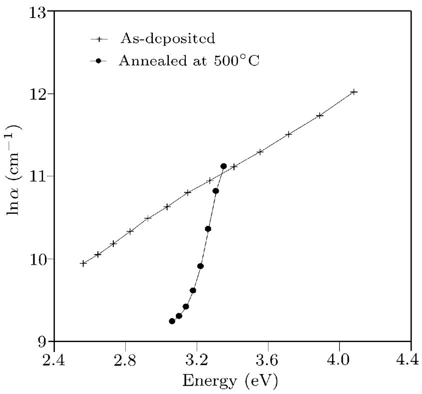

Fig. 8. Semi-logarithmic plots of absorption coefficient as a function of energy for as-deposited and annealed zinc nitride films on Corning 7059 glass substrates.

In conclusion, we have investigated the optical and structural properties of a pulsed filtered cathodic vacuum arc deposited (PFCVAD) zinc nitride film on a Corning 7059 glass substrate. Optical measurements are made at wavelength 190–1100 nm. X-ray diffraction studies indicate that zinc nitride has a cubic structure. Annealing makes drastic changes of the optical properties of the film. The optical energy band gap of the films for assuming direct transition increases from 2.91 eV to 3.24 eV with annealing. The optical energy band gap of the films for assuming indirect transition increases from 1.91 eV to 3.06 eV with annealing. The absorption band edge becomes sharper. Optical absorption in the energy range of 1.75 eV–3 eV decreases from 1/2 to 1/6 of unannealed values. The decrease of the extinction coefficient with the increase of the annealing can be related to the change in the transmittance of the films. Defects decrease with annealing. E_0 is found to be 0.74 eV for the as-deposited zinc nitride film and to be 0.14 eV for the film annealed at 500°C. The above results indicate that annealing of the PFCVAD zinc nitride films makes good optical quality.

The structural properties of the semiconducting zinc nitride thin films grown by PFCVAD are not significantly changed but optical properties are changed considerably. Annealing at 500°C for one hour does not make any change of the XRD spectrum. To clarify the increase of the optical energy gap and the optical absorption mechanism, we are performing the IR studies.

The structural and optical qualities of zinc nitride films deposited by using PFCVAD at room temperature are consistent with those of zinc nitride films deposited by using other growth techniques, indicating that the PFCVAD method is very effective in facilitating film growth at room temperatures.

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