Electronic Building and Properties of Aluminum Nitride Irradiated with Ions

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Abstract − The parameters of electronic structure and their influence on properties of aluminum nitride after irradiation with carbon ions and subsequent annealing in vacuum and oxygen were investigated using optical absorption and photoconduction. The influence of annealing conditions on the dominating charge carriers type and on the Fermi level position and on the character of the electronic transitions between the states localized within the forbidden band and the allowed bands were established.

1. Introduction

Expansion of functional possibilities of dielectric materials causes need of regulation of their properties. This is possible, as an introduction of active impurity on stage of fabrications, so by means of irradiation with charging particles. Irradiation by ions, causing a complex of physical-chemical processes, creates in near surface layer of materials new unequillibrium state, distinguished on structured-phase composition and on the contents of defects from initial state. Enumerated changes form an electronic structure of forbidden band of compounds that defines a change of optical and photoelectric characteristics of material, type of charge carriers, energy parameters of conduction σ ($\sigma = 10^{-15}$–10^{-6} S) [1, 2].

Theoretical investigations of electronic structure AlN with aluminum excess have allowed to calculate depending on positions of Fermi level the efficiency to generations anion V_N and cation V_{Al} vacancies, clusters of vacancies $V_{Al} - V_N$, defects of substituting O_N, donor-acceptor complexes $V_{Al} - O_N$, define their charge state under mutual conversions and value with provision for information on identifying defect levels their influence on characteristics. These results were generalized in [3]. In this work explored parameters of electronic structure AlN changed by defects induced by irradiation with ions, and determined influence of annealing on stability of these changes.

2. Experimental

Irradiation of plates AlN was executed in frequency-pulsed mode by carbon ions with the energy of 50–150 keV, density of current in the pulse was 10^{-2}–10^{-3} A/cm^2, fluence was $\Phi = 10^{14}$–10^{17} cm^{-2}. Postimplantation annealing was executed in the vacuum ($P \leq 10$ Pa, $T_{an} = 300$–2000 K) and in the oxygen ($P = 10^5$ Pa, $T_{an} = 300$–800 K). Optical and photoelectrical measurements methods and treatment of results is provided in [1, 3]. Charge state of defects was defined from thermal and photostimulated currents [3] or from thermal depolarization currents. The relative concentration of induced defects N_i/N (N and N_i – concentration of absorbtion centres before and after irradiation and annealing) was valued from absorption coefficient $\alpha(h\nu)$ before and after the irradiation. Absolute value of concentrations the absorption centres N and N_i was defined with the Smacula's formula.

3. Experimental Results and Discussion

In forbidden band (FB) of unirradiated AlN in the energy interval $\Delta(h\nu) = 1.9$–4.5 eV was reveallled the exponential distribution of localized states (LS) induced by defects. Because of high concentration of biographical defects ($N \geq 10^{19}$ cm^{-3}) and strong overlapping corresponding it LS in the material observed interband absorbtion which realized by indirect ($\Delta'(h\nu) = 3.6$–4.5 eV) and direct transitions ($\Delta'(h\nu) = 4.0$–4.6 eV) (Table). The FB width, evaluated for direct ($E_g \leq 3.8$ eV) and indirect ($E_g \leq 2.6$ eV) transitions, is significantly narrowed, comparing to single crystals (5.7–6.3 eV [4–10]). A Fermi level ε_F is situated in FB near intersection of continuously distributed on energy donor and acceptor levels at the energy band $\varepsilon = 2.0$–4.0 eV.

Created by irradiation the induced defects (ID) create in FB an additional LS having a high density. The fluence ions effects on the electronic structure change the most vastly reveals itself in intervals 1.4–2.5, 1.7–2.9 and 2.5–3.3 eV. The accumulation localized states with energy $\varepsilon = 3.2$–4.3 eV and their interaction causes a narrowing FB (Table). Localized donor states with the energy of 1.5–4.2 eV in consequence of accumulation and interaction causing their induced defects are united in subband of powerfully cooperated states. Absorption is formed by the indirect and direct allowed transitions between the subband states and conduction band (CB). With increasing density of subband states and degree of their overlapping probability of realization of direct transition increases. A linear intercoupling between Urbach's energy E_u ($\alpha(h\nu) \sim \exp(h\nu/E_u)$ [1]) and optical transition energy $h\nu$ at constant absorption coefficient α (Fig. 1, curves 1, 2)) and between E_u and E_g ($\Delta'(h\nu) = 3.7$–4.8 и 2.8–3.8 eV, Fig. 1, curves 5, 6) is observed. This indicates on the partial delocalization of the electrons, the partial delocalization of the electrons, occupying subband states.

Table. Parameters of optical absorption of aluminum nitride after irradiation with carbon ions and annealing (approximation in intervals Δ(*h*ν) by Urbach's law $\alpha(h\nu) \sim \exp(h\nu/E_u)$ and in intervals Δ′(hν) by law $\alpha \cdot h\nu \sim (h\nu - E_g)^m$ for direct ($m = 1/2$) and indirect ($m = 2$) allowed transition through optical gap E_g)

Φ, cm^{-2}	Δ(*h*ν), eV	E_u, eV	Δ′(*h*ν), eV	E_g, eV
Until irrad.	1.9–3.7 3.7–4.5	1.4 0.8	3.6–4.5 4.0–4.6*	2.5 3.8*
10^{16}	1.8–3.1 3.7–4.1	0.9 1.1	3.7–4.2 3.7–4.7*	2.1 3.4*
$2 \cdot 10^{17}$	1.4–2.5 2.5–3.3 3.2–4.1	2.1 2.5 4.1	1.4–4.0 2.8–3.5* 3.5–4.2*	0.1 2.4* 2.8*
$2 \cdot 10^{17**}$	1.4–2.4 2.6–4.0	5.6 5.3	1.4–4.7 1.6–2.8*	–1.0 1.2*

* Parameters of direct allowed transitions.
** Annealing in vacuum at T_{an} = 1100 K.

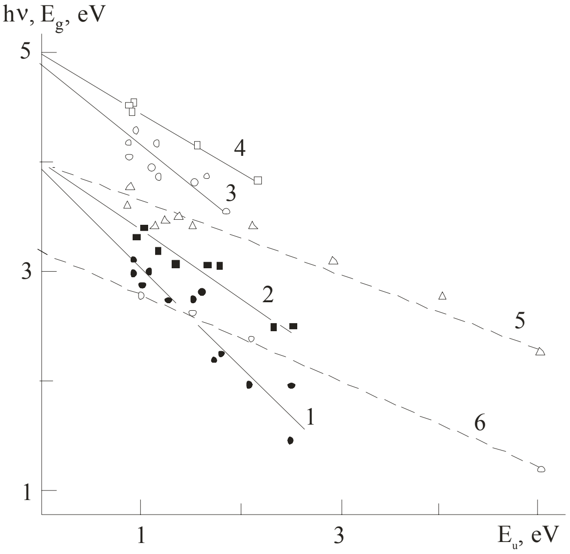


Fig. 1. The dependencies of optical transition energy *h*ν (1–4) at constant values of the absorption coefficient $\alpha = 1.3 \cdot 10^4$ (1), $1.7 \cdot 10^4$ (2), $2.2 \cdot 10^4$ (3), $2.8 \cdot 10^4$ cm^{-1} (4) and optical gap for direct allowed transitions E_g (5, 6) in intervals $\Delta'(h\nu) = 3.7–4.8$ (5) and 2.8–3.8 eV (6) from the Urbach's energy E_u

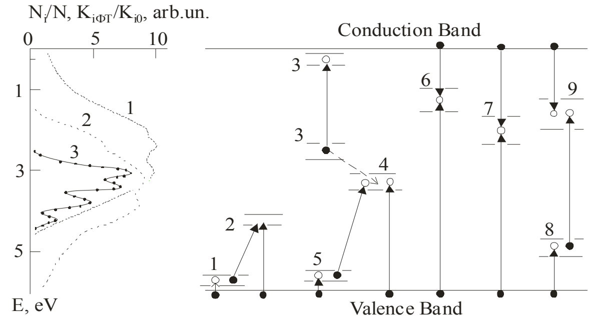
Accumulation of the deep donors states having energy *h*ν = 1.5–3.0 eV within subband defines spectrums relative photosensitivity $K_i/K(h\nu)$ ($K = (\sigma_{h\nu} - \sigma)/\sigma$, $\sigma_{h\nu}$ – photoconduction) most effectively [1]. Influence of the subband states on parameters of interband absorption and correlation between spectrums $K_i/K(h\nu, \Phi, T_{an})$ (σ, $\sigma_{h\nu}$ of the n-type) and $\alpha(h\nu, \Phi, T_{an})$ indicates on partial overlapping between the subband donor states ε_c – (1.5–2.0) eV (ε_c – bottom of conduction band) and the conduction band «tails» with energy ε_c – (0.1–1.8) eV [1]. Analysis of the optical and photoelectrical data allowed us to deduce that Fermi level under conditions $\Phi \geq 10^{17}$ cm^{-2}, $\sigma \geq 10^{-7}$ S ($\sigma_{h\nu}$ n-type) shifted to conduction band on value 1.5–2.0 eV [1].

Postimplantation annealing in the vacuum promotes further electronic structure transformation (levels overlapping degree, optical gap, character of the distribution LS on energy, ε_F position, etc.) and the localized states population with exceeding electrons and holes too. Additional states, cased by impurity-vacancy and interstitial-vacancy complexes, which formed after annealing, change electronic structure parameters in correlation with changing of the interband and intraband (within subband) absorption transition characteristics, photoconduction parameters and stability of properties changes too. Concentration of localized subband states ε_c – (1.5 – 3.3) eV, its population with electrons and degree their cooperation (~ E_u) have maximum after annealing after 1000–1500 K [1]. Fermi level is in addition displaced to CB on values 0.6–1.0 eV for its position in the irradiated material. From changes the parameters of interband absorption and photoconduction was fixed shift of the subband borders on values 0.4–0.6 eV aside high energy (Table). As a result subband strongly cooperated states with energy ε = 1.6–4.6 eV was formed. This subband defines the interband absorption at realization of direct transition into conduction band. The transport charge and photoconduction are realized by the hopping mechanism with alternating length of hop with participation of the subband states ε_c – (1.5–2.3) eV and ε_c – (2.8–3.4) eV. Reduction of optical gap E_g is due to high density LS near the valence band (VB) top ε_v and influence of electronic transitions between these levels and subband levels ε_v + (0.5–2.8) eV.

Significant contribution to electronic structure changes give local levels of the induced defects. On dependencies $h\nu(E_u, \Phi)$ and $E_g(E_u, \Phi)$ stand out three energetic ranges of their influence: 3.0–3.2 eV, 3.8–4.0 eV and 4.7–4.9 eV (Fig. 1). Range 3.0–3.2 eV corresponds to interband optical transitions ($\Delta'(h\nu)$ = = 2.8–3.6 eV) and transitions, forming local photosensitive (n-type of $\sigma_{h\nu}$) bands of absorption with centres at ε_i = 3.2–3.4 eV [3]. Range 3.8–4.0 eV correspond to the direct transitions in the interval $\Delta'(h\nu)$ = 3.7–4.4 eV. Range 4.7–4.9 eV ($\Phi \leq 10^{16}$ cm^{-2}) coincides with the band centre ε_i = 4.8 eV, stipulated by oxygen-contained biographic defects [8–13] and their complexes.

Thus, as a result ion-thermal modification in forbidden band of aluminum nitride are revealled three components of electronic structure: localized states exponential distributed on energy, strongly cooperated into subband donor states and local levels situated near subband and/or levels corresponding to biographic defects. Energy borders of the subband and degree of influence of its levels on characteristics are defined by modification conditions.

Annealing of irradiated with ions AlN in the oxygen allows to define a changing of the parameters of electronic structure in consequence with the introduction oxygen-containing complexes (OCC), forming at adsorptions of oxygen on defect clusters, value a degree of their influence on optical, photoelectrical and electro-physical characteristics. At the accumulation of OCC localized states continuously distributed on energy within subband will converted in the set of strongly localized donors or acceptor levels. These levels reveal itself in the manner of local bands of absorption and photosensitivity in spectrums $N_i/N(h\nu)$ and $K_{i\Phi T}/K_{io}(h\nu)$ (K_{io}, $K_{i\Phi T}$ – photosensitivity before irradiation and after irradiation and annealing in the oxygen) (Fig. 2,a).



a b

Fig. 2. Changing a concentration of absorbing localized states in the forbidden band (1, 2) and relative spectral photosensitivity (3) after irradiating AlN with carbon ions ($\Phi = 10^{17}$ cm^{-2}) and annealing in the oxygen at $P = 10^5$ Pa, $T_{an} = 800$ K, $t \leq 3 \cdot 10^3$ s (1) и $t \geq 3 \cdot 10^3$ s (2, 3) (a). Electronic transitions scheme (b). Photostimulated, thermal activated and recombination transitions are shown by direct arrows, but capture of electrons-dashed arrows

Exchange by electrons between levels of the oxygen-containing complexes and complexes between induced defects lowers the population of subband donors states $\varepsilon_c - (0.1–3.3)$ eV, degree of overlapping these states and photosensitivity n-type. Density of subband donors states is insufficient for realization of direct transitions into conduction band. However, realization of absorption by indirect transitions in interval $\Delta'(h\nu) = 2.8–4.3$ eV promotes an overlapping of acceptor levels created the oxygen-containing complexes ($\varepsilon \geq 3.0$ eV) and levels of biographic defects O_N [3]. An intensity of electronic transitions from the valence band states to acceptor levels, cooperated in subband, increases at the accumulation oxygen-containing complexes. Changes of the parameters α, E_u, Δ, $\Delta'(T_{an}, h\nu)$ were showed on reducing static disorder in the crystalline lattice and on increasing the electron localizations on the levels $\varepsilon_c - (1.5–3.0)$ eV and $\varepsilon_c - (2.7–5.5)$ eV. Also partial recovering an electronic structure of AlN occurs. Analysis of spectrums N_i/N, $K_{i\Phi T}/K_{io}(h\nu, T_{an})$, photo- and thermally stimulated currents (domination p-type of conduction and photoconduction), as well as parameters of levels with $\varepsilon = 0.1–1.2$ eV, defining energy of activations σ and $\sigma_{h\nu}$ ($T = 300–650$ K), have shown that under total concentration oxygen-containing defects and complexes $N_i \geq 5 \cdot 10^{19}$ cm^{-3} Fermi level is shifted from $\varepsilon_F = \varepsilon_v + (3–5)$ eV (n-type conduction and photoconduction [1, 3]) to aside the valence band $\varepsilon_F = \varepsilon_v + (1.8–3.2)$ eV ($\sigma \leq 10^{-12}$ S).

Under annealing in the oxygen parameters of different types of absorption correlate with energetic and kinetic parameters of σ and $\sigma_{h\nu}$. This indicate to the strong influence of levels cased the oxygen-containing defects and complexes on characteristics. Enumerated facts allow with provision for theoretical calculations of electronic structure [4–6] and models [7–13] to define an influence on the absorption and on σ and $\sigma_{h\nu}$ electronic transitions between allowed bands and levels induced by defects and oxygen-containing complexes. Developped scheme of levels and transitions (Fig. 2,b) combined on energy with spectrums N_i/N, $K_{i\Phi T}/K_{io}(\varepsilon, T_{an})$ (Fig. 2,a). Peaks of absorption are close to energy of the photosensitivity levels.

Weak populated levels $1 - \varepsilon_v + (0.1–0.5)$ eV, $2 - \varepsilon_v + (1.6–2.0)$ eV define energies of activation σ, $\sigma_{h\nu}$ with p-type ($\varepsilon = 0.1–0.5$ eV, $T = 300–400$ K) and unstable band with $\varepsilon = 1.8$ eV in spectrums $K_{i\Phi T}/K_{io}(\varepsilon, T_{an})$ at the exchange of electrons with the valence band states (Fig. 2,b). These levels are unstable to annealing in the oxygen and in the vacuum and caused, probably, oxygen-containing complexes on the base existing until irradiation biographic cation vacancies and adsorbed molecules of oxygen.

Accumulation of oxygen-containing complexes with the participation of induced defect clusters ($Al_i–Al_i$ [3]) causes broadening the band 1.9 eV, transformation it in the band 2.2–2.45 eV (Fig. 2a). Analysis of changing the spectrums N_i/N, $K_{i\Phi T}/K_{io}(h\nu, T_{an})$ with provision for band identifications with $\varepsilon = 2.8$ eV (($Al_i–V_N$)-centre [3, 12–14]) has allowed a unstable band 2.2–2.45 eV to connect with transitions electrons between levels Al_i^+-centre $3 - \varepsilon_c - (2.4–3.0)$ eV and $\varepsilon_c - (0.1–0.4)$ eV (Fig. 2,b), which stipulated oxygen-containing complexes on the base induced defects [3]. The electrons transitions from valence band on the acceptor level $4 - \varepsilon_v + (2.5–2.9)$ eV (O_i-centre), emerging in the complex as an acceptor [3, 15, 16], form a band 2.6 eV ($\sigma_{h\nu}$ of p-type) (Fig. 2,a). Weak band of photoconduction at $\varepsilon = 2.2$ eV caused by transition between levels $5 - \varepsilon_v + (0.3–0.5)$ eV and $4 - \varepsilon_v + (2.5–2.9)$ eV belonging to this complex. Instability of parameters of levels 3–5 is caused by their interaction with the subband acceptor levels $\varepsilon_v + (2.2–3.5)$ eV and location ($Al_i…O_i$)-centres on borders an clusters $Al_i–Al_i$ [3].

Weak intensive local band with $\varepsilon_i = 4.8$ eV (Fig. 2,a) is formed by electron transitions from VB on the level $6 - \varepsilon_v + (4.5–5.1)$ eV, caused unstable to annealing in the oxygen the defect O_N [6–9, 12–15].

More strong and clearly localized in spectrums $N_i/N(h\nu,T_{an})$ band with $\varepsilon_i = 3.9$ eV (Fig. 2,a) and band a photosensitivity of p-type with $\varepsilon = 3.7–4.0$ eV ($\sigma \le 10^{-12}$ S) caused by electron transitions from VB on donor level 7 – $\varepsilon_v + (3.8–4.0)$ eV of thermal stable complexes on the base ID (Al_i [3]) and defects of substituting O_N [4–8, 12–16], which answer in FB states with $\varepsilon = 3.2–4.3$ eV ($N_i \ge 10^{19}$ cm^{-3}), forming interband absorption (table). Analysis of changes band parameters with $\varepsilon_i = 3.95$ eV under annealing in the oxygen allows to expect that this band is connected with interstitials and/or vacancy ID. With provision for level identifications $\varepsilon_v + (3.9–4.0)$ eV [4–8, 13] and $\varepsilon_v + (4.1–4.2)$ eV [16] ($O_N^{0(-)}$) and high efficiency forming O_N by $\varepsilon_F = \varepsilon_v + (1.0–3.0)$ eV [4, 16] band 3.95 eV was referred to electron transitions from VB on the level $\varepsilon_v + (3.6–4.3)$ eV of the defect $O_N^{0(-)}$ which bound in the complex with Al_i^+ [3]. Levels 6, 7 render a significant influence on interband absorption by direct ($\Delta'(h\nu) = 2.8–3.8$ eV, 3.7–4.8 eV) transitions (Fig. 1, curves 1–5).

In consequence of electronic–ion reactions between defects and oxygen the defect clusters $V_N – V_N$, $V_{Al} – V_N$ when increasing a temperature will converted in complexes, containing O_N, with change of their charge state, dissociate on single defects and annihilate [3]. Shift ε_F from its positions in the material n-type σ ($\sigma \ge 10^{-7}$ S) under $\varepsilon_F = \varepsilon_V + (3.0–5.0)$ eV in lower half FB as a result accumulations OCC and subband donor levels $\varepsilon_c – (1.5–4.2)$ eV compensations, enlarges efficiency of formation V_N and O_N, but velocity of generations ($V_{Al} – O_N$)-centres is lowerred [4, 16]. Coexistence under annealing in the oxygen processes of formation and dissociation of the ($V_{Al} – O_N$)-centres determine the instability of parameters LS, answerring band 3.3–3.6 eV (Fig. 2,a). Spectrums N_i/N, $K_{i\Phi T}/K_{io}(h\nu, T_{an})$ and identification of optical centres [7–11] and instability of band show that it is formed by transition between acceptor 8 – ε_v +
+ (1.1–1.3) eV and donor 9 – $\varepsilon_v + (4.0–4.2)$ eV levels of complexes [3]. Analysis of spectrums photosensitivity p-type allows band 2.9 eV to connect with intracenter transitions of electrons between levels 8 and 9. Exchange by electrons between VB and level 8, trapping the holes, defines the energy of activation (0.5–0.9 eV at $T \ge 500$ K) $\sigma_{h\nu}$ of p-type [1]. Donor levels 6, 7, 9 capture electrons from CB, causing reduction of conductivity n-type and $\sigma_{h\nu}$ of p-type in the band $\varepsilon = 3.2–4.0$ eV (Fig. 2,b).

Thus, oxygen-containing complexes, formed in modified with ions AlN after annealing in the oxygen, create in FB continuously set LS and separate levels and define the changes of the optical and photoelectrical characteristics. At the accumulation of concentrations OCC and increasing interaction between forming their defects the Fermi level is fixed in the lower half of FB in consequence of compensating influence acceptor complex on donor subband levels.

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