A New View on the Nature of Electron Levels in Amorphous Silicon Nitride

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Abstract

A new view on the nature of shallow and deep levels in amorphous silicon nitride (a-Si_3N_4) which is used as thin layers in microelectronics and solar energetics is present. A self-consistent diagram of the electron levels of defects in the forbidden gap of silicon nitride is built up. A non-contradictory model is proposed that describes the mechanism of write-in and erasure in integral nonvolatile memory devices based on the metal − nitride − oxide − semiconductor structures. Silicon cation radicals bonded with three nitrogen atoms in the (a-Si_3N_4) matrix and lying by 1.6 eV above the bottom of the conduction band are proposed to be considered as deep traps for electrons. Silicon anion radicals which are by 1.8 eV above the top of the valence band are considered as deep traps for holes. This approach allows to eliminate the contradiction between the results of investigations into electrophysical and paramagnetic properties of (a-Si_3N_4). On the basis of the diagram of electron levels and electron-vibrational transitions observed in the luminescence spectra and luminescence excitation spectra of silicon nitride, there arises the possibility to consider the mechanism of phototransformations in (a-Si_3N_4) under the action of UV radiation, for example the luminescence fatigue phenomenon (decrease of its intensity). A hypothesis concerning the nature of shallow electron traps near the bottom of the conduction band of (a-Si_3N_4) has been put forward.

INTRODUCTION

Amorphous silicon nitride has been extensively used in microelectronics. Thin ($0.1–1.0$ μm) films of this compound are used as active medium of electrically alterable nonvolatile memory devices based on the metal − nitride − oxide − semiconductor (MNOS) structures [1]. As insulating layers, amorphous Si_3N_4 (further referred to as a-Si_3N_4) is used in thin-film transistors based on amorphous hydrogenized silicon, in power transistors on GaAs, in the elements transforming solar energy into electricity based on MNOS structures [2]. The layers are mainly synthesized by chemical interaction of monosilane with ammonium both at high temperatures (i 700 ºC) and at lower ones (till 100 ºC). The decrease of synthesis temperature is usually achieved by the transformation of the mixture $SiH_4 : NH_3 > 10$ into chemically active plasma due to the energy of high-frequency electromagnetic fields. As a rule, stoichiometric (N : Si = 1.33) layers or those with excess nitrogen are used in microelectronics [2].

Electronic properties of (a-Si_3N_4) are determined mainly by deep traps which are the centres of electrons and holes trapping, as well as by shallow traps which are responsible for the spreading of charge captured by deep traps; in other words, they are responsible for the degradation of nonvolatile memory devices based on MNOS. Because of this, a correct knowledge about the nature of levels is extremely important in selecting the technology for the preparation of layers intended for specific application.

The investigation of the properties of deep traps was carried out by different methods. First of all, we should mention depolarization measurements of MNOS capacitor structures. It was reliably stated [1] that:

1) electron traps are situated 1.6 eV lower the bottom of the conduction band while the hole traps are 1.8 eV above the top of valence band;

2) both kinds of traps possess very large capture sections (about 10^{-14} cm^2) which is characteristic of single-charged centres with non-screened Coulomb potential;

3) concentrations of electron and hole traps in amorphous layers of silicon nitride, not subjected to any action after they were synthesized, are identical and equal to ~ $3 \cdot 10^{19}$ cm^{-3} while the concentration of neutral paramagnetic centres is about two orders of magnitude smaller [3]. Because of this, a-Si$_3$N$_4$ can be considered as dielectric compensated by deep donor and acceptor levels [1].

Theoretical investigations of electronic structure [4, 5], numerous ESR investigations [2], the studies of luminescence properties [6−8] were dedicated to the determination of the nature of deep traps in a-Si$_3$N$_4$. It was stated by means of ESR that:

1) practically independent of a-Si$_3$N$_4$ preparation method and further action of UV light, gamma quanta or ions, a paramagnetic centre (K-centre [2]) is always detected in the system. This is a silicon atom with an unpaired electron and zero charge (dangling bond) $\equiv$Si$\cdot^0$;

2) this centre becomes diamagnetic after an electron or a hole is captured;

3) under the action of UV light upon the MNS (metal − nitride − silicon) structure the concentration of paramagnetic silicon radicals increases together with the increase of positive charge in silicon nitride which is observed as hysteresis $\Delta V+$ at the voltage-capacitance $C − V$ dependence [9].

We believe that the question concerning the nature of traps in a-Si$_3$N$_4$ should be discussed in terms of radical chemistry. According to theoretical notions [4, 5], neutral silicon radical acts as a deep trap formed as a result of $\equiv$ Si — H or $\equiv$ Si — Si $\equiv$ bond breakage. The authors of [4, 5] believe that the paramagnetic silicon centre $\equiv$Si^0 is able to capture both holes and electrons. In other words, this is a deep amphoteric level situated 3.1 eV above the top of the valence band. In this case, when positive potential is applied to the metal electrode of the MNOS structure, the $\equiv$Si$\cdot^0$ radicals (dangling bonds) should capture electrons; when negative potential is applied, they should capture holes transforming into the cation $\equiv$Si$\cdot^\oplus$ or anion $\equiv$Si$\cdot^\ominus$ radicals, respectively.

It is easy to note that there is an evident contradiction between model considerations of the authors of [2−5] and electrophysical data. First, depolarization measurements with the MNOS structures definitely show that in (a-Si$_3$N$_4$) there are the traps of both types, for holes and for electrons, their depth being different. Second, the traps are initially charged; they exhibit large sections of charge carries capture. Third, the initial concentration of silicon paramagnetic centres in (a-Si$_3$N$_4$) is more than an order of magnitude smaller ($< 10^{18}$ cm^{-3}) than the concentration of deep traps determined by the electrophysical method [3]. Finally, under the UV action, the charge in (a-Si$_3$N$_4$) increases in phase with the number of paramagnetic centres [9]. If the neutral radical $\equiv$Si$\cdot^0$ is a trap, its concentration should decrease as charges are captured but not increase.

The goal of the present work is to create an adequate non-contradictory model that will describe the functioning of nonvolatile memory device based on silicon MNOS structures, to build up a self-consistent diagram of electron transition levels in a-Si$_3$N$_4$, to explain, on this grounds, the mechanisms of write-in and erasure in nonvolatile memory devices, and the mechanisms of phototransformations in a-Si$_3$N$_4$ under UV irradiation.

EXPERIMENTAL

Silicon nitride films for our experiments were obtained from the plasma composed of the mixture of monosilane with ammonia (NH$_3$: SiH$_4$ ~ 20) at a temperature of 190 °C and a pressure of ~ 10^{-2} Torr, on the substrates made of silicon, indium and gallium arsenides and on quartz plates treated according to a standard procedure. Film thickness was ~ 300 nm, n was about 1.8 (λ = 632.8 nm). Thus prepared a-Si$_3$N$_4$ possesses the same set of traps as silicon nitride used in the nonvolatile memory devices [2, 4].

Transmission, luminescence and luminescence excitation spectra were recorded at room temperature. Transmission spectra were recorded according to a single-ray technique within the spectral range of 200−380 nm. A hydrogen-deuterium lamp LDD-400 (400 W) was used as irradiation source. This lamp pro-

vides a continuous spectrum which is most intensive in short-wave UV region. The reference sample was a quartz substrate similar to that on which the silicon nitride film was deposited. The samples were placed outside the exit slit of MDR-23 monochromator. The light was collimated by quartz optics and registered by a FEU-100 photomultiplier. The inlet and outlet slits were identical when recording transmittance. They were 100 μm each and were not changed during scanning. The reverse linear dispersion of MDR-23 is 1.3 nm/mm for the diffraction grating 1200 lines/mm operating in the first order. Optical density and absorption spectra were calculated from transmission spectra.

Luminescence spectra were recorded using a modified complex of the KSVU-23 type with two MDR-23 monochromators. The replicas of diffraction grating (1200 lines/mm) for the region of 200−1000 nm were mounted in monochromators. In order to exclude superposition of higher-order spectra, band filters were used. The LDD-400 lamp was used to excite luminescence. The receivers were photomultipliers of the FEU-100 type with the spectral sensitivity region of 170−850 nm, and FEU-79 which is more sensitive in the red spectral region. The

latter was cooled to −20 ℃. Calibration over wavelengths was carried out with the help of a mercury-helium low-pressure lamp of the DRGS-12 type. No correction was performed for luminescence and excitation spectra.

RESULTS AND DISCUSSION

Since the recombination of charge carriers occurs at deep levels [7], one could expect that electron transitions with the energy corresponding to the positions of these levels in the forbidden gap of a-Si_3N_4 would manifest themselves. Figure 1 shows luminescence spectra of amorphous silicon nitride. Maxima are observed at 1.6 and 1.8 eV. This is an additional, besides electrophysical data [1], confirmation of the existence of two trapping centres but not one as it was postulated in [2−4]. One of the centres is for holes and another for electrons. It is most reasonable to remove the contradiction between electrophysical and luminescence data, on the one hand, and theoretical calculations and ESR data on another hand, by building up a non-contradictory model of write-in and erasure in nonvolatile memory device based on MNOS structures.

On the ground of the above, we believe that it is most correct to consider silicon ion radicals with a fixed charge as traps: cation radicals $\equiv$Si·$^{\oplus}$ as electron traps and anion radicals $\equiv$Si·$^{\ominus}$ as hole traps. When positive potential is applied to the metal electrode of the structure, electron are tunnelling from silicon through a thin (20−100 Å) layer of silicon dioxide and are captured by positively charged traps within silicon nitride volume:

$$\equiv\text{Si·}^{\oplus} + \ominus \ \rightarrow \ \equiv\text{Si·}^{(+-)} \tag{1}$$
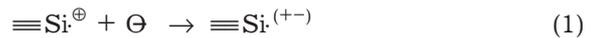
Having captured an electron, diamagnetic cation radicals are transformed into neutral paramagnetic exciton radicals $\equiv$Si·$^{(+-)}$. Since a-Si_3N_4 is compensated by deep traps, a negative charge of ~ $3\cdot10^{19}$ cm^{-3} arises due to anion radicals within the same film volume. The charge is equal to the number of formed neutral centres. The charge exhibits itself as DV^- hysteresis in $C - V$ plots of the capacitor MNOS structures. When a negative potential is applied to the metal electrode, the reaction reverse to
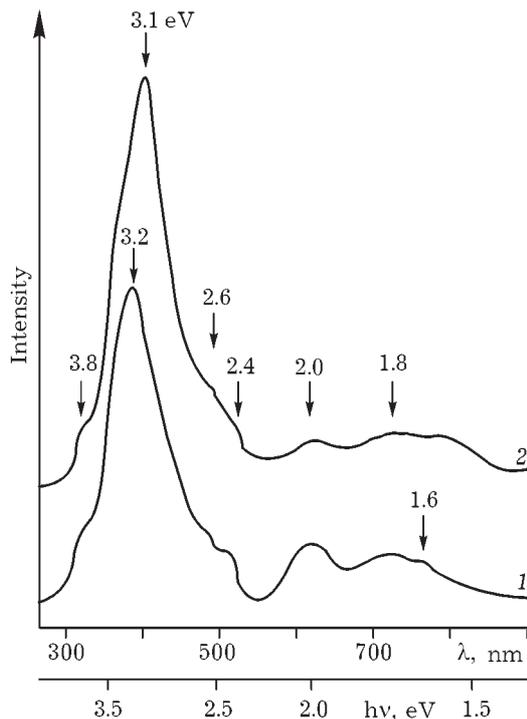
Fig. 1. Luminescence spectra of a-Si_3N_4/GaAs recorded at 300 K: $1 - l_{exc}$ = 267 nm, hn = 4.6 eV; $2 - \lambda_{exc}$ = 243 nm, hv = 5.1 eV.

(1) occurs. Exciton radicals are decomposed into cation radicals and electrons:

$$\equiv Si\cdot^{(+-)} \rightarrow \ \equiv Si\cdot^{\oplus} \ + \ominus \tag{2}$$
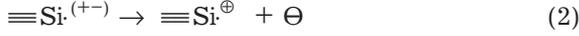
The balance between anion and cation radicals in a-Si_3N_4 is thus recovered and the dielectric film becomes again neutral.

When a negative potential is applied to the metal electrode, holes are captured by anion radicals:

$$\equiv Si\cdot^{\ominus} + \oplus \rightarrow \ \equiv Si\cdot^{(+-)} \tag{3}$$
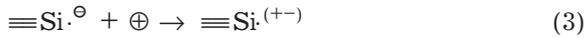
Neutral exciton radicals are formed. Due to the disturbance of the balance between ion radicals with opposite charges, excess cation radicals (~ $3\cdot10^{19}$ cm^{-3}) appear in a-Si_3N_4. These cation radicals form a positive charge, and $\Delta V+$ appears in $C-V$ plots which is the evidence of charge accumulation. The change of potential polarity of the MNOS structure leads to the decomposition of silicon exciton radicals with the formation of anion radicals and holes, and the recovery of charge balance in a-Si_3N_4:

$$\equiv Si\cdot^{(+-)} \rightarrow \ \equiv Si\cdot^{\ominus} + \ \oplus \tag{4}$$

The storage of information, *i.e.* constant character of the charge captured by deep traps in case when the powerpack of the memory device based on MNOS is switched off, is conditioned by the stability of silicon ion radicals $\equiv Si\cdot^{\oplus}$ and $\equiv Si\cdot^{\ominus}$. As experience shows, the charge can be conserved in the memory device for many months [1].

According to theoretical considerations [4, 5], silicon paramagnetic radical is higher than the top of the valence band by 3.1 eV. As Fig. 1 shows, the corresponding maximum in the luminescence spectrum is observed along with the 3.2 eV maximum. We consider both these transitions to be connected with the neutral paramagnetic silicon centre. The first one among them is the intragap transition

$$\equiv Si\cdot^{(+-)} \ (3.2 \text{ eV})$$
$$\rightarrow \ \equiv Si - Si \equiv \ (0.1 \text{ eV}) + h\nu \ (3.1 \text{ eV}) \tag{5}$$
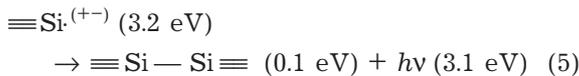
and the second one is the transition

$$\equiv Si\cdot^{(+-)} \ (3.2 \text{ eV})$$
$$\rightarrow \text{ valence band} + h\nu \ (3.2 \text{ eV}) \tag{6}$$
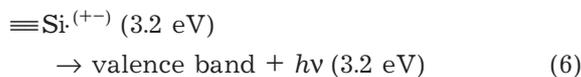
Thus, we confirm a theoretical conclusion of [4]

that a diatomic silicon cluster $\equiv Si - Si \equiv$ is 0.1 eV above the top of the valence band but we do not confirm the conclusion of [5] by the same author that the $\equiv Si - Si \equiv$ defect is 0.5 eV below the top of the valence band.

It should also be noted that the knowledge of the paramagnetic silicon centre as a triply coordinated neutral silicon radical is ambiguous. This centre can be easily imagined to be a triply coordinated silicon atom within silicon nitride lattice with dangling bond formed after the $\equiv Si - N \equiv$ bond is broken. It has been proved in [6] by means of IR spectroscopy that this process occurs. Then, the addition of a neutral particle, an exciton, to this radical does not change the charge state of the radical and consequently the paramagnetic state. To the contrary, the localization of charge on the radical with unpaired electron turns it into a diamagnetic centre. The necessity to introduce an exciton radical into the model naturally follows from the comparison between experimental data obtained by means of ESR and the results of electrophysical measurements, or $C-V$ characteristics of the MNOS structures [9], as well as from the fact that the initial deep traps are single-charged [1]. It should also be noted that in our model the key part is played by the balance between positively and negatively charged deep traps in a-Si_3N_4.

The consideration of deep traps as diatomic silicon clusters $\equiv Si - Si \equiv$ [1, 6] whose energy is, according to some calcualtions [2], 0.1 eV above the top of the valence band, and according to other calculations [4], outside the limits of the forbidden gap is somewhat strange. The concentration of excess silicon in the stoichio- metric a-Si_3N_4 or in low-temperature one where, *vice versa*, nitrogen excess is observed, would be most probably at the level of ~ $10^{16}-10^{17}$ cm^{-3}.

When a charge of ~ 10^{-1} C·cm^{-2} passes through a-Si_3N_4, the degradation of its polarization, depolarization and conduction properties is observed. This is manifested in the decrease of charge captured during the polarization of the MNOS structure and increase of the quasistationary conduction and the rate of charge spread. The same degradation phenomena are observed in a-Si_3N_4 under irradiation with UV light with the quanta energy
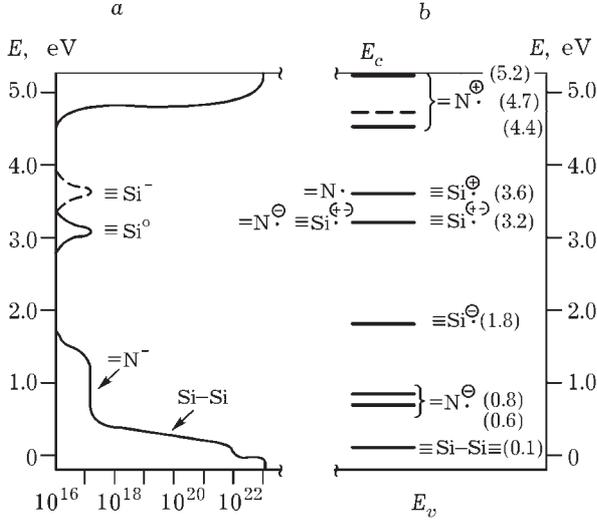
Fig. 2. The diagram of state density and the positions of energy levels of the defects in the forbidden gap of a-Si$_3$N$_4$: a − calculation [4], b − our data.

$h\nu \geq 5.0$ eV. After the irradiation dose becomes more than the threshold value, $W_{thr} > 1.5 \cdot 10^{25}$ photons/cm^3 [10], degradation changes in silicon nitride result in breakdown. On the other hand, $\cong 5 \cdot 10^{19}$ cm^{-3} metastable paramagnetic nitrogen anion radicals $\equiv\!\!=\!\!N^{\cdot\ominus}$ appear in amorphous Si$_3$N$_4$ [4, 11]. According to [7], this is exhibited in photoluminescence spectra as the disappearance of the transition in green spectral region at $h\nu \cong 2.5$ eV. In our studies we observed two intragap transitions: $h\nu_1 \cong 2.4$ eV and $h\nu_2 \cong 2.6$ eV (see Fig. 1). This means that shallow traps for holes (Fig. 2, a) are distributed over two maxima. According to the calculations [4], the tail of shallow states stretches from valence band to ~ 1.5 eV. In order

to build up a self-consistent diagram of electron levels in a-Si$_3$N$_4$, we attribute the positions of 0.8 and 0.6 eV to these levels (see Fig. 2, b). Two levels of nitrogen anion radical arise because the bonds $=\!\!N\!\!-\!\!H$ and stressed $\equiv\!\!Si\!\!-\!\!N=$ break similtaneously under UV irradiation [7]. In both cases, metastable paramagnetic radicals $\equiv\!\!N^{\cdot\ominus}$ are formed. However, they exist in different surroundings and their energy positions should also be different.

Figure 3 shows absorption spectrum. Interference hinders the determination of E_g, as well as the observation of shallow levels located near the bottom of the conduction band. The calculation of the energy gap, E_g was carried out according to the Tautz equation [12] over the edge of fundamental absorption within the range of $5.5-6.2$ eV where the absorption coefficient changes from ~ $1.0 \cdot 10^4$ to $4 \cdot 10^4$ cm^{-1}. Figure 3 shows that at the energy of ~ 5.6 eV a fracture is observed on the curve which does not allow to use the whole measured region in the calculations. The calculation of E_g for each region separately gives ~ 4.7 and ~ 5.17 eV, respectively. The latter seems more acceptable since it is known from literature that optical width of the forbidden gap for low-temperature plasmochemical a-Si$_3$N$_4$ is within the range of $5.1-5.3$ eV [1, 4, 5, 13].

The width of the forbidden gap can also be estimated from the luminescence excitation spectrum (Fig. 4) using the maximum related to the highest energy. The difference by 0.21 eV compirises two vibration quanta of the bond $\equiv\!\!Si\!\!-\!\!N=$ (840 cm^{-1}) [1, 7]. On the
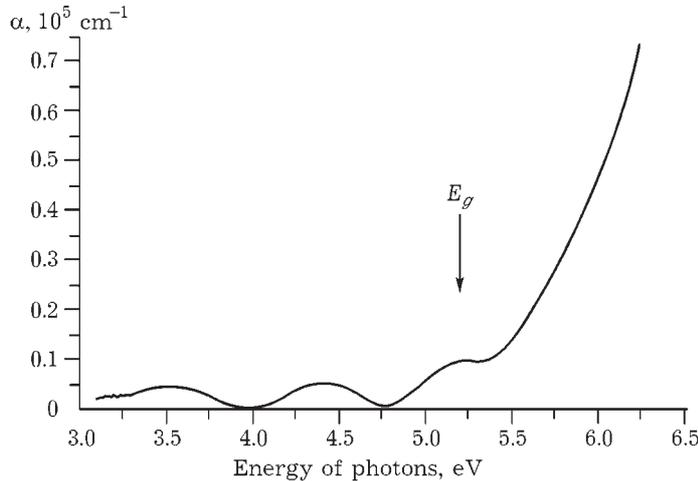
Fig. 3. Absorption spectrum of a-Si$_3$N$_4$ film on quartz substrate (d = 300 nm, T = 300 K).
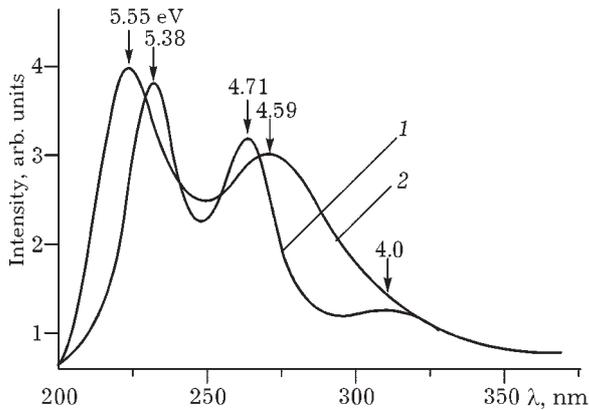
Fig. 4. Luminescence excitation spectra (λ_{max} = 400 nm) at 300 K: 1 − a-Si$_3$N$_4$ film on quartz substrate, d = 300 nm; 2 − β-Si$_3$N$_4$ polycrystal.

other hand, the very fact of the observation of clearly exhibited maximum is the evidence of the presence of localized electron state near the bottom of the conduction band. We suppose that two other levels in luminescence excitation spectra are also shifted higher energies in comparison with the position which could be manifested in the absorption spectrum.

It is known from IR spectra [1, 7] that in a-Si$_3$N$_4$ stoichiometric for silicon to nitrogen ratio only stretching vibrations of the bonds $\equiv$ Si —N $=$ and $=$N — H are detected. Because of this, localized state can be attributed to nitrogen doubly coordinated with silicon ($\equiv$ Si)$_2$N—H. However, since the corresponding maximum is also observed in polycrystal silicon nitride where hydrogen is definitely absent, this shallow level should be attributed to nitrogen dangling bond $\equiv$ Si — N· — Si $\equiv$. The second maximum corresponding to shallow level of nitrogen subsystem is also present both in amorphous and polycrystal silicon nitride and is shifted by 0.31 eV which corresponds to three vibration quanta of the $\equiv$ Si — N $=$ bond (2520 cm^{-1}). This means that the electron level in absorption spectrum should be 4.4 eV above the top of the valence band. Thus, the latter two levels are most likely related to shallow traps near the bottom of conduction band. The presence of shallow traps in this region is confirmed by electrophysical measurements [1] and theoretical considerations [4].

The nature of shallow traps for holes was considered in literature [4, 5] as nitrogen anion radicals but no hypotheses were ever put forward concerning the nature of shallow traps for

electrons. The studies of degradation phenomena by multiple switching on and off ($> 10^6$) revealed that the character of the relaxation of charge accumulated on deep traps is identical both for electrons and for holes. This means that the positions of the levels corresponding to shallow traps, over which the charges of both signs spread, with respect to allowed bands are practically identical.

We suppose that the traps for electrons can be nitrogen cation radicals $=$N·$^{\oplus}$ that are formed during the breakage of $=$N—H and $\equiv$ Si — N $=$ bonds followed by the capture of holes by nitrogen radicals. The capture of electrons and holes should occur at equal probabilities, so the tails of shallow electron states near the allowed bands should be symmetric. Finally, the shift of the third maximum which is absent in the spectrum of polycrystal silicon nitride can be unambiguously related only to the vibration quanta of the $=$N—H bond (3340 cm^{-1}). It follows from the above that a deep electron level which is 3.6 eV above the top of valence band should be exhibited in absorption spectra. It coincides with the radiative recombination level of silicon cation radical $\equiv$Si·$^{\oplus}$.

We assume that this coincidence leads to the interaction between the silicon and nitrogen subsystems. We also assume that with respect to nitrogen subsystem this level is recombination one. The recombination of nitrogen atom containing unpaired electron, which is formed after the breakage of $\equiv$ Si — N $=$ or $=$N—H bonds, with free electron occurs on this level. The recombination process results in the formation of anion radical $\equiv$N·$^{\ominus}$. It should be noted that the vibration quantum of the $=$N—H bond is practically the same as four vibration quanta of the $\equiv$ Si — N $=$ bond. Energy transfer (0.4 eV) from the nitrogen subsystem to silicon one can occur *via* radiationless transition from the level 3.6 to 3.2 eV through the formation of the complex $\equiv$Si·$^{(+-)}$$=$N·$^{\ominus *}$ followed by anion radical phosphorescence [7].

Taking the above into account, one can build a self-consistent diagram of electron levels in amorphous silicon nitride. The diagram is shown in Fig. 2, b. For comparison, Fig. 2, a

Fig. 5. Energy levels and electron transitions in a-Si$_3$N$_4$.

shows state density distribution over the forbidden gap of a-Si$_3$N$_4$ [4].

Using these results and luminescence spectra, we have built up the electron transition diagram for a-Si$_3$N$_4$ (Fig. 5). It helps to explain the mechanisms of phototransformations under UV irradiation. For example, let us consider the phenomenon of photoluminescence fatigue (the decrease of luminescence intensity during prolonged irradiation of the sample). As it was stated in [11], the intensity of emission of the 2.5 eV band falls down to zero starting from the dose of ~10^{20} cm^{-2}. At the same time, ~ 10^{20} cm^{-3} paramagnetic nitrogen centres appear in the same sample. This phenomenon is reversible, i. e. the luminescence of the 2.5 eV band is recovered after thermal annealing of the samples, for example, at ~ 350 $^{\circ}$C for 30 min or light quanta $h\nu$ = 2.5 eV irradiation. According to [11], the reason of luminescence fatigue is the transformation of radiative recombination centres into nonradiative paramagnetic ones. When radiative recombination centres are completely consumed, luminescence intensity becomes zero. The mechanism of this phenomenon can be described with the help of the diagram (see Fig. 5). Under the action of light quanta ~ 5.0 eV

$$\equiv Si — N \equiv + h\nu (\cong 5.2 \text{ eV})$$
$$\rightarrow [\equiv Si\cdot] + \equiv N\cdot^{*} (\cong 5.2 \text{ eV}) \qquad (7)$$

$$\equiv N—H + h\nu (\cong 5.2 \text{ eV})$$
$$\rightarrow [H] + \equiv N\cdot^{*} (\cong 5.2 \text{ eV}) \qquad (8)$$

upon a-Si$_3$N$_4$, the breakage of stressed $\equiv Si — N \equiv$ and $\equiv N—H$ bonds occurs: Here $\equiv N\cdot^{*}$ is the excited nitrogen diamagnetic radical with an unpaired electron at the level of 5.2 eV (energy is measured from the top of the valence band). At room temperature, silicon radical and proton are close to their initial position (cage effect).

According to the electron transition diagram (see Fig. 5), after the breakage of bonds, excited nitrogen radicals pass to the recombination level of 3.6 eV emitting the quantum of 1.6 eV. At this level they recombine with free electrons

$$\equiv N\cdot^{*} (\cong 5.2 \text{ eV})$$
$$\rightarrow \equiv N\cdot (\cong 3.6 \text{ eV}) + h\nu (1.6 \text{ eV}) \qquad (9)$$

$$\equiv N\cdot (\cong 3.6 \text{ eV}) + \ominus \rightarrow \equiv N\cdot^{\ominus *} (\cong 3.6 \text{ eV}) \qquad (10)$$

turning into nitrogen paramagnetic anion radicals:

According to the diagram (see Fig. 5), recombination with electron leads to nonradiative transition from the 3.6 eV level to 3.2 eV followed by the emission of light quantum with the energy of 2.6 eV. This refers to the $\equiv N\cdot^{*}$ radical which is formed as a result of $\equiv N—H$ bond breakage. The formation of $\equiv N\cdot^{\ominus *}$ anion radical from the $\equiv Si — N \equiv$ bond is accompanied by the emission of a 2.4 eV light quantum. Anion radicals pass to metastable levels of 0.6 and 0.8 eV, respectively. The total concentration of stressed bonds $\equiv Si — N \equiv$ and $\equiv N—H$ is equal to the concentration of arising nitrogen paramagnetic centres [11]. This means that the irradiation with the dose of ~ 10^{20} cm^{-2} leads to a complete consumption of initial bonds and the radiative recombination luminescence in this region falls down to zero, luminescence fatigue occurs.

At room temperature, metastable paramagnetic radicals $\equiv N\cdot^{\ominus}$ disappear within two or three weeks [7, 11]. This process can be accelerated by thermal or photo annealing of the degraded a-Si$_3$N$_4$, and all the initial properties of the dielectric (concentration of stressed bonds $\equiv Si — N \equiv$ and $\equiv N—H$, diamagnetic properties and luminescence) are completely recovered. Activation energy for annealing is $\cong$ 0.1 eV. The same value has been obtained for

thermal annealing of the samples subjected to electric degradation [1]. The recovery mecha-

$$\equiv N^{\cdot\ominus} \ (\cong 0.6 \text{ eV}) + h\nu(\cong 2.5 \text{ eV}) + [H]$$
$$\rightarrow \ \equiv N\text{—}H + \ominus \ + \Delta Q \ (\cong 3.1 \text{ eV}) \qquad (11)$$
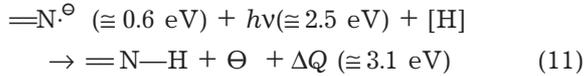
nism, for example for $\equiv$ N—H bonds under the action of light, can be represented as follows: One can see from this equation that the heat ΔQ released in the reverse process is close to the $\equiv$ N—H bond strength which is $\cong 3.35$ eV [1].

CONCLUSION

A self-consistent model of write-in and era-sure in nonvolatile memory devices has been proposed. It allows to bring to agreement the known data on the nature of deep traps reported in electrophysical, ESR, photoluminescent and theoretical studies. Silicon ion radicals $\equiv Si^{\cdot\oplus}$ and $\equiv Si^{\cdot\ominus}$ are the most proper candidates for the deep traps. These ion radicals are present in amorphous silicon nitride in equal concentra-tions. This is the difference of the proposed model from that reported in [2−5] where an amphoteric monocentre is assumed as deep trap (a silicon radical with unpaired electron) which contradicts to the data of electrophysical and luminescence studies. On the basis of the model one can explain: 1) a huge electron and hole capture section observed in the depolari- zation bstudies of the MNOS structures [1], 2) small initial concentration of neutral paramagnetic centres on silicon which increases with UV irradiation in phase with positive charge, 3) the presence of radiative recombination centres with the energies of 1.6, 1.8 and 3.2 eV in lumi-nescence spectra. On the basis of absorption, lu-minescence and luminescence excitation spec-tra of a-Si_3N_4, a self-consistent diagram has been built up for energy levels and electron transitions. Using this diagram one can explain the mechanisms of different phototransfor-mations, for example luminescence fatigue phenomenon. It is shown that the structural re-arrangement in a-Si_3N_4 observed by means of ESR in combination with photolumi- nescence [11] and IR spectroscopy [7] is the break- age of $\equiv$ N—H and stressed $\equiv$ Si —N$\equiv$ bonds under UV irradiation.

A hypothesis concerning the nature of shal-low electron traps near the bottom of the con-duction band of a-Si_3N_4 is put forward. Me-tastable nitrogen radicals $\equiv N^{\cdot\oplus}$ can serve as these traps.

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