PERGAMON

Solid State Communications 118 (2001) 129–134

solid state communications

www.elsevier.com/locate/ssc

EPR-study of nitrogen implanted silicon nitride

A.I. Shames[a,*], V.A. Gritsenko[b], R.I. Samoilova[c], Yu.D. Tzvetkov[c], L.S. Braginsky[b], M. Roger[d]

[a]*Department of Physics, Ben-Gurion University of the Negev, P.O. Box 653, 84105 Be'er-Sheva, Israel*
[b]*Institute of Semiconductor Physics, 630090, Novosibirsk, Russia*
[c]*Institute of Chemical Kinetics and Combustion, 630090, Novosibirsk, Russia*
[d]*DRECAM, SPEC, Orme des Merisiers, CEA, Saclay, 91191 Gif sur Yvette Cedex, France*

Received 17 January 2001; accepted 6 February 2001 by P. Burlet

Abstract

Electrons and holes localized in amorphous silicon nitride (Si_3N_4) were studied by electron paramagnetic resonance (EPR). No EPR signals due to localized charges were observed in charged samples, containing high density of traps — almost stoichiometric Si_3N_4. N-implanted Si_3N_4 samples, characterized by a lower density of traps, also showed no corresponding EPR signals. The possible pairing of charges due to antiferromagnetic exchange interactions arising from resonant quantum tunneling has been proposed to explain the absence of signals in samples with high density of traps. We briefly describe various models of spin-pairing including a Wigner glass of bipolarons, with a pair of charges trapped at neighboring traps, and discuss them in connection with the experimental data. © 2001 Published by Elsevier Science Ltd.

Keywords: A. Semiconductors; D. Exchange and Superexchange; E. Electron paramagnetic resonance

PACS: 61.72.Ww; 33.35.Ex; 71.55.Jv; 71.45.Gm

1. Introduction

Amorphous silicon nitride (Si_3N_4) and silicon oxide (SiO_2) remain the two key dielectrics in modern semiconductor devices [1,2]. It is known that Si_3N_4 possesses a high density of traps ($N \sim 10^{21}$ cm^{-3}) and has the property to localize injected charges (both electrons and holes) for a very long time (about 10 years) at room temperature (~300 K). The typical density of charged traps, occupied by electrons (or holes) for Si_3N_4 is $n_t \sim 5 \times 10^{18}$ cm^{-3} [3]. The effect of electron and hole localization in Si_3N_4 is widely used in electrically erasable read-only memory (EEPROM) silicon devices [4].

A lot of effort was made in understanding the origin (atomic and electronic structure) of charge traps in Si_3N_4. The most popular model of such a trap is an amphoteric threefold coordinated silicon atom $\equiv Si\cdot$ with unpaired electron [5–7]. Here symbols (–) and (·) mean a normal chemical bond and an unpaired electron, respectively. According to this model, silicon nitride samples in their initial, non-charged state must be paramagnetic. However, in the previous experiments done on non-charged Si_3N_4 samples, no EPR signals were detected [8,9]. It was shown theoretically that the creation of the pair of charged diamagnetic defects $\equiv Si:$ (negatively charged) and $\equiv Si$ (positively charged) via the reaction $\equiv Si\cdot + \cdot Si\equiv \rightarrow \equiv Si: + Si\equiv$ is energetically unfavorable [7,10,11]. In Ref. [12] the model of diamagnetic neutral $\equiv Si–Si\equiv$ bond was proposed as the defect which is responsible for the localization of carriers in Si_3N_4. This model explains the absence of EPR signal in non-charged silicon nitride. Quantum chemical simulation predicts the appearance of EPR signal after the localization of electron (or hole) by Si–Si bond [13]. In contrast to this prediction, EPR experiments on corona-polarized Si_3N_4 films also show the absence of EPR [8,9]. For the explanation of the latter experimental fact, spin coupling due to the resonant quantum tunneling of localized spins on occupied traps through unoccupied traps was proposed [12]. This model supposes a high density of neutral traps (~10^{21} cm^{-3}) in silicon nitride.

According to the aforementioned model, the spin

* Corresponding author. Fax: +972-7-6472903.
E-mail address: sham@bgumail.bgu.ac.il (A.I. Shames).

0038-1098/01/$ - see front matter © 2001 Published by Elsevier Science Ltd.
PII: S0038-1098(01)00059-X

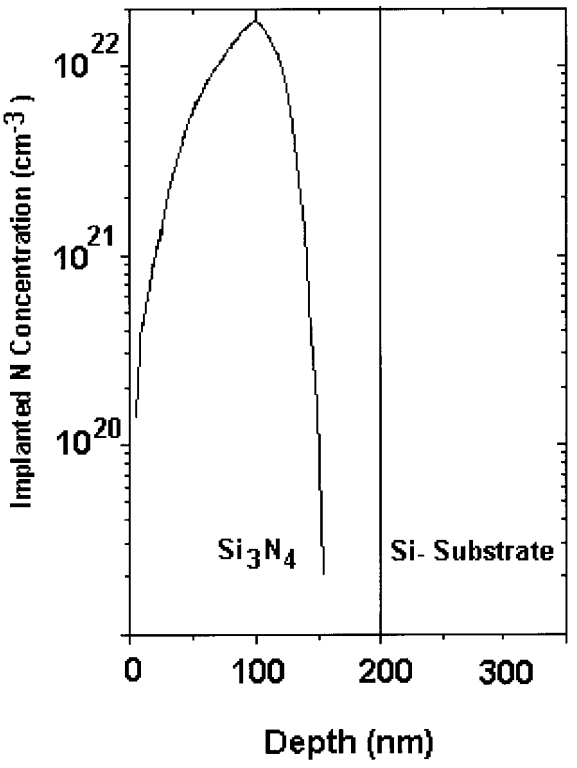

Fig. 1. Distribution of implanted nitrogen in silicon nitride film obtained by TRIM.

coupling occurs due to the electron exchange through traps situated at typical distances of $a \sim N^{-1/3} \sim 10$ Å. This coupling is governed by the hopping frequency of a charge to a neighboring trap and it should decrease exponentially with the distance a between neighboring traps. Hence, in samples with lower concentration of traps, this coupling should decrease rapidly. Isolated localized charges, which cannot take part in the exchange because of long distances between neighboring traps, will occur and the appearance of an EPR signal belonging to non-coupled carriers is expected. The objective of the present study is the EPR investigation of localized electrons and holes in polarized Si_3N_4 samples in which the density of memory traps has been reduced by nitrogen implantation.

2. Experimental

According to the Mott octet rule 8-N, the interaction of nitrogen atoms with Si–Si bonds breaks those bonds followed by the creation of energetically much favorable Si–N bonds according to the reaction [14]

$$3\text{Si–Si} + 2\text{N} = 2\text{Si}_3\text{N} \quad (1)$$

This reaction was used in Refs. [14,15] to explain the removal of hole traps in the process of the silicon oxide nitridation. In the present study the nitrogen implantation was used to remove part of the existing traps (Si–Si bonds) in silicon nitride, aiming to decrease the neutral traps density, and creation of diluted density of localized spins, respectively.

Si_3N_4 2000 Å films were obtained by chemical vapor deposition from dichlorsilane (SiH_2Cl_2) and ammonia (NH_3) on a silicon substrate at 730°C. Low doped high resistivity (150 $\Omega\,cm^{-1}$) n-type silicon wafer (111) orientation was used as a substrate. High resistivity substrate is obligatory for both, growth of the sensitivity of the weak EPR signals' detection and suppression of the EPR signal from free carriers in silicon. The implanted nitrogen dose was $10^{17}\,cm^{-2}$ and the implantation energy was 50 keV. After the nitrogen implantation all samples were annealed for 30 min in dry nitrogen at 750°C to remove radiation defects. Fig. 1 shows the implanted nitrogen distribution in Si_3N_4 on Si substrate, obtained by TRIM program. The maximal concentration of the implanted nitrogen was about $2 \times 10^{22}\,cm^{-3}$. Supposing the Si–Si bond density in silicon nitride is $10^{21}\,cm^{-3}$, the higher ($10^{21}\,cm^{-3}$) implanted nitrogen density results, according to Eq. (1), in removal of Si–Si bonds in nitride. That implanted nitrogen was distributed at distances between ~30 and ~150 nm from the top surface. Therefore, we expected that, within this region, the Si–Si bond density in silicon nitride was decreased by the nitrogen implantation. It is very difficult to get more detailed information on the Si–Si bonds (traps) distribution in N-implanted Si_3N_4.

Injection of electrons and holes into dielectrics was made using corona discharge as described in Refs. [8,9]. Voltage of 3 kV was used at both plasma polarities. The current during corona discharge was about 1 μA. Control of the charge injection into SiO_2 and Si_3N_4 samples was done by capacitance–voltage (C–V) measurements at 100 kHz with In electrode before and after samples' polarization.

EPR measurements were performed on Bruker ELEXYS E-500 and EMX-220 X-band CW digital spectrometers at room temperature ($T = 297$ K) using Bruker ER 4102ST rectangular cavities. Si-based samples of $4 \times 7 \times 0.3\,mm^3$ were placed into an EPR silent Wilmad 5 mm o.d. quartz tube and centered within the cavity. In addition to EPR measurements being done at room temperature, the cavity was also equipped with thick wall quartz Dewar insert aiming to reach the higher sensitivity of the EPR spectrometer. EPR signal search and spectra recording were done using 100 kHz magnetic field modulation of 0.02–0.1 mT, 50–200 μW incident microwave power and slow pass multi-scan acquisition (number of scans $n = 256$ or 1024) mode. Typical acquisition times were 4 or 16 h. The g-values were determined using metallic Li in LiF, exposed by neutron beams ($g = 2.0023 \pm 0.0001$) and 10^{-6} M water TEMPOL solution ($g = 2.0059 \pm 0.0001$), placed in a thin capillary tube together with the sample under study. The latter and a Bruker standard Weak Pitch sample ($\rho_{pc} \sim 10^{13}$ paramagnetic centers cm^{-1}) were used for the

estimation of real spectrometer's sensitivity. Processing of EPR spectra was done using Bruker WIN-EPR software.

3. Results

EPR spectra of initial (before the N-implantation) Si_3N_4 samples showed very weak EPR signal with $g = 2.0054$ and $\Delta H_{pp} = 0.39$ mT which was the same for both non-polarized sample and films containing 5×10^{12} electrons (holes) cm^{-2} (as estimated by C–V). The signal observed originates from triply coordinated silicon atoms with unpaired electron, $Si_3Si\cdot$, and associates with mechanical and growth defects in amorphous silicon and on the surface of crystalline silicon [16]. No other EPR signals were detected even at very long acquisition times ($\sim$16 h, $n = 1024$). This result confirms previously obtained data on the absence of EPR signals in silicon nitride films [8,9].

N-implanted Si_3N_4 samples also showed the absence of any EPR signal from the localized charges. As it is clearly seen in Fig. 2, no signal may be practically distinguished from the noise for the non-polarized sample (Fig. 2a) as well as for samples polarized by positive corona (5×10^{12} electrons cm^{-2}) — Fig. 2b, and negative corona (5×10^{12} holes cm^{-2}) — Fig. 2c. Very weak signal with $g = 2.0054$ was observed for a sample with localized holes. As was mentioned before, this signal belongs to mechanical defects and has no resemblance with signals from localized carriers. Since N-implanted samples passed double annealing, the concentration of those defects was found to be lower than in non-implanted samples.

These negative results on the observation of EPR signal in Si_3N_4 put a question on the detectability of signals produced by the aforementioned amount of localized carriers ($\sim 10^{12}$ spin). Such signals were successfully observed in previous EPR studies of localized carriers in Si-based systems [8,13]. However, it was very important to check the actual experimental set aiming observation of weak signals with $\Delta H_{pp} \sim 0.1$–0.2 mT. The absolute sensitivity of spectrometers in use was estimated as $S_a \sim 10^{11}$ spin mT^{-1}. When taking into account current experimental conditions (low non-saturated incident power, decrease in Q-factor because of dielectric losses, etc.), the real sensitivity seemed to be lower. Fig. 2d shows the EPR spectrum of weak pitch sample ($g = 2.0028$, $\Delta H_{pp} = 0.14$ mT) containing about 10^{13} spins, recorded at the same experimental conditions like Si_3N_4 samples. One can clearly see that such a spectrum reaches signal-to-noise ratio S/N > 3 at quite small number of scans $n = 64$. The weaker signal with $g = 2.0005$, $\Delta H_{pp} = 0.09$ mT is due to the thermal defects in fused quartz of the sample tube. The same S/N ratio was obtained measuring 60 μl sample of 10^{-6} M TEMPOL solution, which also corresponds to $\sim 10^{13}$ spin per one triplet component (spectrum not shown). Based on these experiments one can conclude that the quantity of localized spins of about 10^{12} should be reliably detected under experimental conditions in use.

4. Discussion

Room temperature EPR signals from 10^{11}–10^{12} localized charges have been successfully observed for various Si-based systems [8,11,13]. On the other hand, as it was

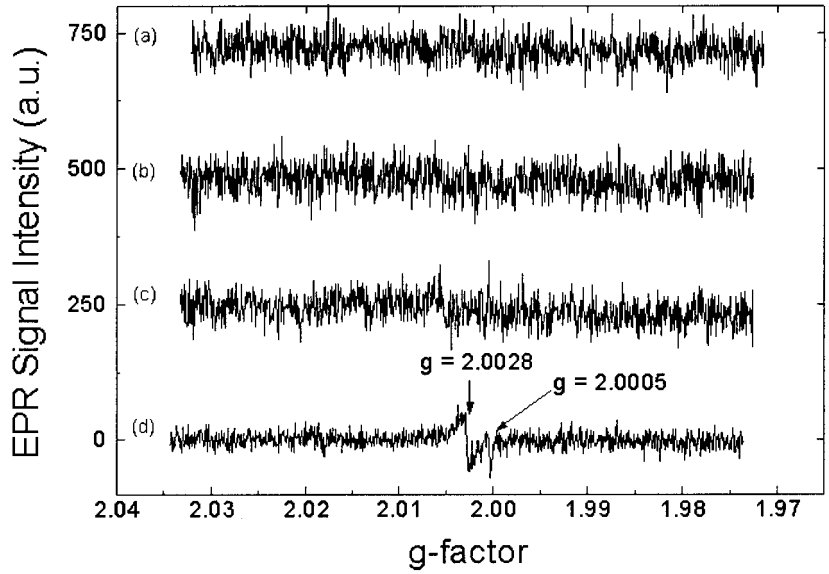

Fig. 2. Room temperature EPR spectra of (a) non-polarized N-implanted Si_3N_4 film ($n = 256$, $\nu = 9.238$ GHz); (b) N-implanted Si_3N_4 film containing injected 5×10^{12} electrons cm^{-2} ($n = 256$, $\nu = 9.243$ GHz); (c) N-implanted Si_3N_4 film containing injected 5×10^{12} holes cm^{-2} ($n = 256$, $\nu = 9.243$ GHz); (d) Weak Pitch test sample containing about 10^{13} spins ($n = 64$, $\nu = 9.243$ GHz).

mentioned above, the life-times of localized charges in Si_3N_4 are extremely long ($\sim 10^8$ s). Both these facts allowed us to rule out any other reasons for the non-detection of the EPR signals (like very short relaxation- and/or life-times, etc.) except for an antiferromagnetic coupling. Let us now investigate various physical processes for a possible antiferromagnetic coupling of localized charges which could suppress the EPR line at $T \sim 300$ K.

1. The simplest one is the trapping of two charges with opposite spins at the same trap site. This mechanism was first proposed by Anderson [17]. It may occur in the case of the polaron energy shift W, due to the distortion of the atomic subsystem, overcomes the strong on-site Coulomb repulsion U, that is paid for putting to charges on the same site. The reaction

$$\equiv Si–Si\equiv \rightarrow \equiv Si\cdot + \cdot Si\equiv \rightarrow \equiv Si : + Si\equiv$$

has been invoked as a preamble for the capture of a pair of electrons or hole on the same site. However, theoretical calculations made by several groups, using such different methods as "MINDO/3" numerical simulations [10], Monte-Carlo calculations [11], and first-principle density functional theory [7], all indicate that the aforementioned reaction is energetic ally unfavorable.

2. An appealing idea has been recently conjectured by one of us [12]. When the density of traps ($\sim 10^{21}$ cm^{-3}) is much higher than the density of charges ($\sim 10^{18}$ cm^{-3}), the localized charges might order among possible traps in some imperfect "Wigner crystal". (Due to the highly disordered aspect of the trap positions, the name "Wigner glass" might be more relevant.) Resonant exchange coupling J between two charges at a distance of about 50 Å might occur via successive hopping through neighboring traps at a much smaller distance ~10 Å. Let us, however, put some order of magnitude to see if this coupling could really explain the absence of any EPR signal at such a high temperature as $T \sim 300$ K. If the absence of the EPR signal at room temperature results from a collective antiferromagnetic long-range order of this imperfect "Wigner crystal", this implies that the exchange coupling J/k_B is of the order of 300 K. In this exchange model, the energy J is smaller than $h\gamma$, where γ represents the hopping frequency from one trap to a neighboring empty trap at 10 Å, which mediates the exchange process of two charges at 50 Å (h is the Planck constant). We conclude that the characteristic time for hopping from one trap to a neighboring trap should then be smaller than:

$$\tau = \gamma^{-1} \ll h/J \sim h/(k_B 300\ \mathrm{K}) \sim 10^{-13}\ \mathrm{s}.$$

This requirement is in strong contradiction with the experimental fact that localized charges stay inside the sample for 10 years $\sim 10^8$ s. With such small characteristic times (of order τ) hopping processes would simply allow the trapped charges to move rapidly towards the interfaces.

Si_3N_4 is a highly polarizable medium. The surrounding atoms are appreciably displaced around a trapped charge and polaronic effects (which were not taken into account in the previous paragraph) play certainly an important role in the process of charge localization. The concept of a "self-trapped" polaron was first introduced by Landau and Froelich, and further discussed by Mott and Gurney [18]. Polaron interactions in many polaron systems have been widely discussed. For a strongly interacting system such an interaction may be attractive, due to the fact that, when a polaron is formed, another charge is attracted by the lattice deformation around the polaron. This leads to the formation of "bipolarons" (polaron pairs) [19]. We have emphasized in a previous paragraph that the on-site Coulomb repulsion U is probably too strong to allow the trapping of a pair of charges on the same site. The smaller repulsion $V \ll U$ between two charges at a distance of the order of 10 Å will not exclude, nevertheless, the possibility of the formation of bipolarons with two charges localized on neighboring traps. Due to the "Anderson superexchange" mechanism, these two charges are coupled antiferromagnetically through exchange interactions. Let us roughly evaluate the order of magnitude of the exchange coupling between two charges at a distance of 10 Å, trapped in a bipolaron state on two neighboring traps within a crude model. For a charge trapped in a polaron state, the electrostatic potential created by the displacements of the surrounding atoms at sufficiently large distance $|r|$ is from Ref. [18]:

$$v_1(r) = -e^2/(4\pi\epsilon_0\kappa_p|r|), \tag{2}$$

where $\kappa_p = 1/(\kappa_\infty^{-1} - \kappa_0^{-1})$ is the effective polaron dielectric permittivity ($\kappa_p \sim 10$ in Si_3N_4). We now consider, in the one-dimensional model schematized in Fig. 3, two polarons at $x_1 = -a/2$ and $x_2 = a/2$, where $a = 10$ Å represents the mean distance between two traps. Not too close from x_1 and x_2, the double-well electrostatic potential is from Eq. (2):

$$v_{12}(x) = -e^2[|x - x_1|^{-1} + |x - x_2|^{-1}]/(4\pi\epsilon_0\kappa_p) \tag{3}$$

(see the thin curve in Fig. 3). Close to x_1 and x_2, the trap potential is schematized by a square well of width ~2.6 Å, which roughly corresponds to the length of a weak Si–Si bond in Si_3N_4.

From the experimental results [20,21], the energy E of one electron in a trap lies in the range -1.3 to -2.0 eV. Let us take the lower bound $E = -1.3$ eV. The corresponding ground-state level E of the trapped charges is shown in Fig. 3. It cuts the double well potential $v_{12}(r)$ at $x_1' = -0.74\ a/2$ and $x_2' = 0.74\ a/2$.. We shall consider that from x_1' to x_2', the potential seen by one electron is roughly described by Eq. (3). Within WKB approximation, the hopping frequency corresponding to the tunneling of an electron from x_1 to x_2 is:

$$t \sim E_0^k \exp\left[-\frac{1}{\hbar} \int_{x_1'}^{x_2'} \sqrt{2m(v_{12}(x) - E)}\,\mathrm{d}x \right] \tag{4}$$

where $v_{12}(x)$ is given by Eq. (3); m is taken as the bare

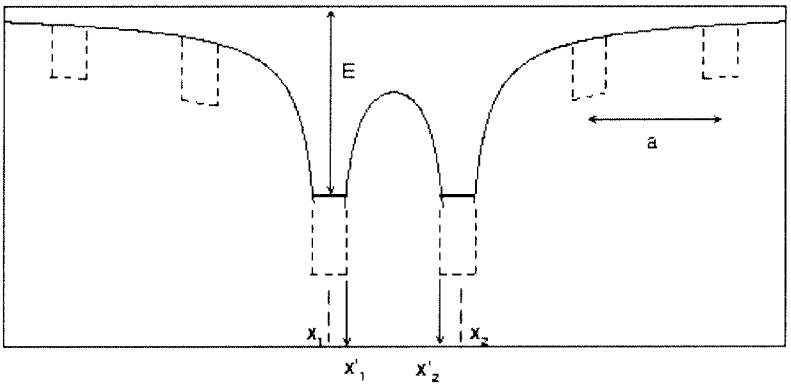

Fig. 3. Bipolaron model. The thin curve corresponds to the polaron electrostatic potential [Eq. (3)] created by two charges localized on neighboring traps at x_1 and x_2. The dashed lines represent the potential, close to the center of trap. Two empty traps are sketched on both sides of the bipolaron well. The mean distance between traps is $a = 10$ Å. The ground state level of electrons in traps $E \sim -1.3$ to -2 eV is represented by a broad black line.

electron mass and the prefactor E_0^k is of the order of the kinetic energy of the electron in the trap (i.e. a few eV).

The antiferromagnetic exchange energy J between two charges at x_1 and x_2 is obtained from the "Anderson super-exchange" mechanism:

$$J = 2t^2/U,$$

where U represents the on-site Coulomb energy paid for putting two electrons at the same site (see above). Taking (to fix the ideas) $U = 4$ eV and $E_0^k \sim 2$ eV, we obtain:

$$J \sim 0.02\ eV \sim 230\ K,$$

which is the right order of magnitude to interpret the absence of EPR signal at 300 K. Note that this estimation is very rough. The one-dimensional calculations drastically underestimate the exchange frequency with respect to the three-dimensional problem. We have taken m as the free electron mass, just because we have no precise data on the effective mass of the electron in these deep traps. The measured value $m^* \sim 0.4m$ concerns the bottom of the conduction band that lies far above. The correct value might be intermediate and lead to even higher values of J. This underestimation, however, could be compensated by the fact that we chose the lower limit for $|E|$ i.e. 1.3 eV (experimental measurements give $|E| \sim 1.3$ to 2 eV).

We conclude that the formation of "bipolarons" with charges on neighboring traps might explain the absence of an EPR signal at room temperature in Si_3N_4 with high density of traps. It could also contribute to the long lifetime (10 years) of trapped charges. The bipolaron (i.e. two electrons + polarization cloud) has a large effective mass and its probability to move to another pair of neighboring empty traps is extremely weak.

Nevertheless, by reducing the density of traps n_t, i.e. the mean distance a between traps, the antiferromagnetic coupling between a pair of charges should decrease exponentially. For sufficiently low uniform density of traps, this exchange interaction should be smaller than 300 K and the EPR line at room temperature should appear.

The negative results obtained in our study are difficult to interpret definitively. As it is shown in Fig. 1, the density of implanted nitrogen and, consequently, the density of traps, is not uniform. We cannot rule out the possibility that during the corona discharge, charges are localized preferentially in the regions where the implantation dose is weak and the density of traps remains high. If the fraction of uncoupled individual charges localized in the middle of the sample (where the implanted nitrogen density is high) is much lower than 10^{12} cm^{-2} (which corresponds to our estimated sensitivity), we cannot observe any EPR signal from those charges.

The structure of Si–Si weak bonds in ^{29}Si implanted SiO_2 is expected to be similar. Some pioneering EPR investigations have been performed on such systems by Kalnitsky and coauthors [13]. In some samples, they do observe a weak EPR signal coming from charged centers located in the region with low ^{29}Si implanted dose (i.e. low density of traps) which, in our opinion, might correspond to uncoupled individual charges, in agreement with our interpretation. We are now performing further EPR investigations of SiO_2 systems implanted by various doses of ^{29}Si.

Acknowledgements

This work has been performed under INTAS grant 97-347.

References

[1] V.A. Gritsenko, Structure and electronic properties of amorphous dielectrics in silicon MIS structures, Science (1993) 280.

[2] Y. Shi, X. Wang, T.P. Ma, IEEE Trans. Electron Devices 16 (1999) 362.
[3] V.A. Gritsenko, E.E. Meerson, I.V. Travkov, Yu.V. Goltvjanskii, Microelectronics (Sov) 16 (1987) 42.
[4] I. Fujiwara, H. Aozasa, A. Nakamura, Y. Komatsu, Y. Hayashi, Proc. IEDM 98, p. 995.
[5] F.R. Libsch, M.H. White, Solid-State Electron. 33 (1990) 105.
[6] P.M. Lenahan, D.T. Krick, J. Kanicki, Appl. Surf. Sci. 39 (1989) 392.
[7] G. Pacchioni, D. Erbetta, Phys. Rev. B 61 (2000) 15005.
[8] W.L. Warren, J. Kanicki, J. Robertson, E.H. Poindexter, P.J. McWhorter, J. Appl. Phys. 74 (1993) 4034.
[9] V.A. Gritsenko, Yu.N. Novikov, Yu.N. Morokov, H. Wong, Microelectron. Reliab. 38 (1998) 1457.
[10] V.A. Gritsenko, Yu.N. Morokov, Yu.N. Novikov, J.B. Xu, cond-mat/0011435.
[11] V.A. Gritsenko, A.D. Milov, JETP Lett. 64 (1996) 531.
[12] V.A. Gritsenko, JETP Lett. 64 (1996) 520.
[13] A. Kalnitsky, J.P. Elul, E.H. Poindexter, P.J. Kaplan, R.A. Lux, A.R. Boothroyd, J. Appl. Phys. 67 (1990) 7359.
[14] V.A. Gritsenko, H. Wong, J.B. Xu, R.M. Kwok, I.P. Petrenko, B.A. Zaitsev, Yu.N. Morokov, Yu.N. Novikov, J. Appl. Phys. 86 (1999) 3234.
[15] V.A. Gritsenko, J.B. Xu, I.H. Wilson, R.M. Kwok, Y.H. Ng, Phys. Rev. Lett. 81 (1998) 1054.
[16] G.K. Walters, T.L. Estle, J. Appl. Phys. 32 (1961) 1854.
[17] P.W. Anderson, Phys. Rev. Lett. 34 (1975) 953.
[18] N.F. Mott, R.W. Gurney, Electronic Processes in Ionic Crystals, Dover, New York, 1964 (and references therein).
[19] G. Wellein, H. Roeder, H. Fehske, Phys. Rev. B 53 (1996) 9666 (and references therein).
[20] V.A. Gritsenko, E.E. Meerson, I.V. Travkov, Yu.V. Golvyanskii, Microelectronika 15 (1987) 92.
[21] S. Manzini, J. Appl. Phys. 62 (1987) 249.