Charge Transport Mechanism in Metal–Nitride–Oxide–Silicon Structures

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*Abstract—***A charge transport mechanism in double oxide–nitride dielectric was studied experimentally and theoretically. We have found that widely accepted Frenkel effect or thermally assisted tunneling could not explain experimental current-field-temperature dependences. For the first time we demonstrate that ionization mechanism of deep traps, which control charge transport in silicon nitride, is due to multiphonon process.**

*Index Terms—***Dielectric materials, EEPROM, MNOS devices, silicon nitride, trap.**

I. INTRODUCTION

THE TRIPLE oxide–nitride–oxide (ONO) and double

oxide–nitride (ON) dielectrics are widely used in silicon

short-transported and ON structures include devices. The advantages of ONO and ON structures include low pinhole density, high dielectric constant, low leakage current, and high breakdown field. Electron and hole capture by deep traps in silicon nitride $Si₃N₄$ of ONO are exploited in electrically erasable read only memory (EEPROM) devices [1]–[4]. In dynamic random excess memory (DRAM) ONO or ON dielectric are used in memory capacitor [5]. ONO structures are also used as insulator in floating gate EEPROM [6] and as interpoly-Si and gate insulator in CMOS devices [7].

It is important to know charge transport mechanism in $Si₃N₄$ especially for SONOS, floating gate EEPROM, and in DRAM. In EEPROM nitride trap ionization defines the charge retention time. In DRAM-based on ONO and ON structures, leakage current must be small for information saving during refreshing.

In fact, charge transport in ONO and ON is controlled by deep traps in $Si₃N₄$. It is widely accepted that in high temperature regime trap ionization mechanism in $Si₃N₄$ is Frenkel effect [8], [9]. However, the fitting of the experimental data on the base of Frenkel effect gives unphysical low the attempt to escape factor in the range $10^6 - 5 \times 10^8 \text{ s}^{-1}$ [10], [11]. Therefore, other trap ionization mechanism should be introduced into consideration, as, for example, the thermally assisted tunneling (TAT) [12], [13] or multiphonon assisted electron detrapping [14], [15].

The goal of the present paper is experimental and theoretical study of charge transport mechanism in $Si₃N₄$ of stacked ON

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dielectric when transport is limited by trapped charge in nitride. By obtained experimental data we examined TAT, and multiphonon assisted ionization models. We have found that only the last mechanism shows a good agreement with the experiment for reasonable physical parameters.

II. SAMPLES

As substrate silicon n-type with resistivity of 7.5 Ω cm was used for MNOS structures fabrication. Tunnel oxide (18 Å) was thermally grown on silicon at 740°C. LPCVD silicon nitride with thickness of 530 Å was prepared at 760° C. The ratio of $SiH_2Cl_2/NH_3 = 0.1$. Al electrodes with square $5 \cdot 10^{-3}$ cm² were made with photolithography.

III. THEORETICAL MODEL

A one-dimensional (1-D) and one band model of charge transport is used, which takes into account Shockley–Reed statistics for trap population. In the case of our experiment, when positive bias was applied on Al electrode, one band transport model assumes only electron injection from silicon substrate and neglects the hole injection from Al electrode [16]. In fact, the barrier for hole injection from Al gate into $Si₃N₄$ (2.5 eV) is larger than the one for electron on the interface $Si-Si₃N₄$ (2.0 eV, see [17]). Moreover, the thin oxide between Si and $Si₃N₄$ facilitates the electron injection because of electric field amplifying in oxide due to the low dielectric constant of oxide ($\varepsilon = 3.9$) in comparison with one of nitride ($\varepsilon = 7$). Under these assumptions, electron transport in $Si₃N₄$ can be described by the following set of equations:

$$
\frac{\partial n(x,t)}{\partial t} = -v \frac{\partial n(x,t)}{\partial x} - \sigma v n(x,t) (N_t - n_t(x,t)) + n_t(x,t) P(x,t)
$$
\n(1)

$$
\frac{\partial n_t(x,t)}{\partial t} = \sigma v n(x,t) (N_t - n_t(x,t))
$$

$$
- n_t(x,t) P(x,t) \tag{2}
$$

$$
\frac{\partial F(x,t)}{\partial x} = -\frac{en_t(x,t)}{\varepsilon \varepsilon_0}.\tag{3}
$$

Here n, N_t , and n_t are densities of free electrons, electron traps, and occupied traps, respectively. $F(x, t)$ is the local electric field, e is the electron charge, σ is the cross section of the trap, v is an electron drift velocity, and $\varepsilon = 7$ is a low-frequency dielectric constant of $Si₃N₄$. P is the probability of trap ionization per second.

Presently it is widely accepted that charge transport in $Si₃N₄$ at high temperatures ($T > 200$ K) is described by Frenkel effect [9], [10], [13], [17]–[19] and for this model the trap ionization probability P is given by

$$
P = \nu \exp\left(-\frac{W - \beta\sqrt{F}}{kT}\right); \quad \beta = \sqrt{\frac{e^3}{\pi \varepsilon_{\infty} \varepsilon_o}}.\tag{4}
$$

Here, W is the trap energy, β is Frenkel constant, $\varepsilon_{\infty} = 4.0$ is the high-frequency $Si₃N₄$ dielectric constant, ν is an attempt to escape factor. Obviously Frenkel model cannot describe trap ionization at low temperature, where tunnel mechanism of electron escape dominates. Therefore in the present paper we investigate two models, which are able to describe of trap ionization in entire temperature region.

One of these models is the thermally assisted tunnel (TAT) detrapping, which was proposed in [12], [13]. We use the following modification of this model when the trap ionization probability is given:

$$
P = \frac{\nu}{kT} \int_0^{W-\beta\sqrt{F}} \cdot dE \exp\left(-\frac{E}{kT} - \frac{2}{\hbar} \int_{x_1}^{x_2} dx \sqrt{2m^*(eV(x) - E)}\right) + \nu \exp\left(-\frac{W - \beta\sqrt{F}}{kT}\right)
$$

$$
(x) = W - \frac{e}{4\pi\varepsilon\varepsilon_0 x} - Fx,
$$

$$
x_{1,2} = \frac{1}{2} \frac{W - E}{eF} \left(1 \mp \left(\frac{eF}{\pi \varepsilon \varepsilon_{\infty} (W - E)^2} \right)^{1/2} \right) \tag{5}
$$

 \boldsymbol{V}

for Coulomb potential. Here, E is the excited energy level, and m^* is the tunnel effective mass. Unlike paper [18] we assume a continual distribution of excited electron levels for thermally assisted tunneling. One can see that this model coincides with Frenkel model in high temperature limit and also describes the pure tunnel ionization at low temperature (see Fig. 1).

The second model of carrier detrapping we consider is the multiphonon trap ionization [14], [15]. Theory of multiphonon processes [15] gives the following equation for the probability of ionization:

$$
P = \frac{eF}{2\sqrt{2m^*W_{opt}}} \exp\left(-\frac{4}{3}\frac{\sqrt{2m^*}}{\hbar eF}W_{opt}^{3/2} + 4\frac{m^*W_{ph}}{\hbar^2}\right)
$$

$$
\cdot \frac{W_{opt}(W_{opt} - W_t)}{e^2F^2} \coth\frac{W_{ph}}{2T}\right). \quad (6)
$$

Here, W_{opt} , W_t are the optical and thermal energies of trap ionization, and W_{ph} is the phonon energy.

IV. RESULTS AND DISCUSSION

Two sets of experiments were performed to obtain the most information about trap ionization mechanism. For the first set the current dependence on temperature was measured and for second one the current as a function of applied voltage was registered. The experimental current dependence on temperature

Fig. 1. Experimental current–temperature dependence at different electric fields (dots) compared with simulation for multiphonon and TAT mechanisms of trap ionization. The rate of temperature decrement is 1 K/s. Best fit parameters: multiphonon mechanism (solid line) $W_t = 1.85$ eV, $W_{opt} = 3.7$ eV, $W_{ph} = 0.064$ eV, $N_t = 7.5 \times 10^{18}$ cm⁻³, $\sigma = 5 \times 10^{-13}$ cm²; TAT (dashed line) $W_t = 1.25$ eV; $m^* = 4$ m_o; $\nu = 10^6$ s⁻¹; $N_t \approx 2.5 \times 10$ cm⁻³; and $\sigma = 5 \times 10^{-13}$ cm⁻³.

Fig. 2. I–V characteristics at different temperatures and positive potential on gate (dots) compared with multiphonon mechanism. Parameters for simulation: $W_t = 1.71 \text{ eV}, W_{opt} = 3.6 \text{ eV}, W_{ph} = 0.064 \text{ eV}, N_t = 1 \times 10^{19} \text{ cm}^{-3},$
and $\sigma = 5 \times 10^{-13} \text{ cm}^2$.

at different fixed positive voltages (on Al) is shown in Fig. 1 in Arrhenius coordinates $\log J - T^{-1}$. Current is approximately constant for the temperature lower than 200 K and increases with temperature in high temperature region ($T > 200$ K). Similar behavior of current was previously observed in [8], [9], [19].

The measured current–voltage $(I-V)$ characteristics are shown in Fig. 2 at different temperatures for positive potential on metal. These graphics demonstrate that current magnitude increases exponentially with the electric field.

For data fitting on the base of TAT, the varied parameters were ν, W, m^* , and N_t , whereas we used fixed $\sigma = 5 \times 10^{-13}$ cm^2 for trap cross-section [18]. The numerical method to solve (1)–(3) is similar to the one described in [20]. The results of simulation are reported in Fig. 1. A satisfactory agreement with experiment can be obtained only for low the attempt to escape factor $\nu = 10^6$ 1/s and abnormal high tunnel effective mass in $Si₃N₄$ for electron $m^* = 4$ m_o. The last contradicts to experimentally measured $m^* \approx 0.5 \, \text{m}_o$ [17], [21], [22].

Fitting results on the base of the multiphonon trap ionization model [see (6)] are presented Figs. 1 and 2 as solid lines. In this case the varied parameters for fitting were: W_{opt} , W_t , W_{ph} . For simulation we used in this case the fixed values $m^* = 0.5$ m_o , trap density N_t , and the same trap cross-section as in TAT simulation. One can see that there is a good agreement between experiment and simulation for all temperature diapason and for all values of applied voltage. Thus, the simulation of both experiments gives close trap parameters. Small difference in these parameters can be related with experimental errors and slow current relaxation phenomenon [23]. Multiphonon model gives the physical reasonable attempt to escape factor value in order of 5×10^{13} s⁻¹ and trap energies $W_t = 1.78 \pm 0.07$ eV.

V. CONCLUSION

In this letter, experimental results of charge transport in SiO_2/Si_3N_4 stacked dielectric were analyzed on the base of two theoretical models. It was found TAT can describe experimental data only with unphysical low attempt to escape factor, and enormously high tunnel effective mass. For these reasons, it appears that this model is not suitable for charge transport in $Si₃N₄$.

In contrast, the model of multiphonon trap ionization satisfactory describes charge transport experiments in $Si₃N₄$. It gives the physical reasonable values for trap parameters. Multiphonon mechanism of trap ionization in silicon nitride should be used for retention simulation in SONOS and floating gate EEPROM.

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REFERENCES

- [1] J. Bu and M. H. White, "Effect of two-step high temperature deuterium anneals on SONOS nonvolatile memory devices," *IEEE Electron Device Lett.*, vol. 22, pp. 17–19, Jan. 2001.
- [2] S. Minami and Y. Kamigaki, "A novel MONOS nonvolatile memory device ensuring 10-year data retention after 10⁷ erase/write cycles," IEEE *Trans. Electron Devices*, vol. 40, pp. 2011–2017, Nov. 1993.
- [3] H. Aozasa, I. Fujiwara, A. Nakamura, and Y. Komatsu, "Analysis of carrier traps in $Si₃N₄$ in oxide/nitride/oxide or metal/oxide/nitride/oxide/silicon nonvolatile memory," *Jpn. J. Appl. Phys.*, vol. 38, pp. 1441–1447, 1999.
- [4] G. O. Lo, S. Ito, D.-L. K. Wang, V. K. Mathews, and P. C. Fazan, "Highly reliable $SiO₂/Si₃N₄$ stacked dielectric on rapid-termal-nitrided rugged polysilicon for high-density DRAM's," *IEEE Electron Device Lett.*, vol. 13, pp. 372–374, July 1992.
- [5] H.-W. Liu and H.-C. Cheng, "Excellent low-pressure-oxidized $Si₃N₄$ films on roughened poly-Si for high-density DRAM's," *IEEE Electron Device Lett.*, vol. 19, pp. 320–322, Sept. 1998.
- [6] S. Mori, "Thickness scaling limitation factors of ONO interpoly dielectric for nonvolatile memory devices," *IEEE Trans. Electron Devices*, vol. 43, pp. 47–53, Jan. 1996.
- [7] T. P. Ma, "Making silicon nitride films a viable gate dielectric," *IEEE Trans. Electron Devices*, vol. 45, pp. 680–690, Mar. 1998.
- [8] S. M. Sze, "Current transport and maximum dielectric strength of silicon nitride films," *J. Appl. Phys.*, vol. 18, pp. 2951–2955, 1967.
- [9] , *Physics of Semiconductor Devices*. New York: Wiley, 1981, pp. 362–430.
- [10] R. A. Williams and M. M. E. Beguwala, "The effect of electrical conduction of $Si₃N₄$ on the discharge of MNOS memory transistors," *IEEE Trans. Electron Devices*, vol. ED-25, pp. 1019–1030, 1978.
- [11] V. A. Gritsenko *et al.*, "Nonstationary electrons and holes transport by depolarization of MNOS structures: Experiment and numerical simulation," *Microelectronics*, vol. 16, pp. 42–50, 1987.
- [12] R. M. Hill, "Pool–Frenkel conduction in amorphous solids," *Philos. Mag.*, vol. 23, pp. 59–86, 1971.
- [13] O. K. Lui and P. Migliorato, "A new generation-recombination model for device simulation including the Poole–Frenkel effect and phononassisted tunneling," *Solid State Electron.*, vol. 41, pp. 575–583, 1997.
- [14] S. S. Makram-Ebeid and M. Lannoo, "Quantum model for phononassisted tunnel ionization of deep levels in a semiconductor," *Phys. Rev. B*, vol. 25, pp. 6406–6424, 1982.
- [15] V. N. Abakumov, V. I. Perel, and I. N. Yassievich, "Nonradiative recombination in semiconductors," in *Modern Problems in Condensed Matter Sciences*, V. M. Agranovich and A. A. Maradudin, Eds. Amsterdam, The Netherlands, 1991, vol. 33.
- [16] A. S. Ginovker, V. A. Gritsenko, and S. P. Sinitsa, "Two band conduction of amorphous silicon nitride," *Phys. Stat. Sol. b*, vol. 26, pp. 489–495, 1974.
- [17] V. A. Gritsenko, E. E. Meerson, and Y. N. Morokov, "Thermally assisted tunneling at $Au-Si_3N_4$ interface and energy band diagram of metal–nitride–oxide-semiconductor structures," *Phys. Rev.*, vol. B 57, pp. R2081–R2083, 1997.
- [18] S. Manzini, "Electronic processes in silicon nitride," *J. Appl. Phys.*, vol. 62, pp. 3278–3284, 1987.
- [19] V. A. Gritsenko and A. V. Rhjanov, "Kinetics of nonequilibrium process related to Frenkel effect in high electric field," *J. Tech. Phys.*, vol. 46, pp. 2155–2161, 1976.
- [20] K. Lehovec and A. Fedotowsky, "Transient charge and current distribution in the nitride of MNOS devices," *IEEE Trans. Electron Device*, vol. ED-24, pp. 536–540, May 1977.
- [21] H. Bachofer *et al.*, "Transient conduction in multidielectric silicon–oxide–nitride–oxide semiconductor structures," *J. Appl. Phys.*, vol. 89, pp. 2791–2800, 2001.
- [22] Y. Shi, X. Wang, and T.-P. Ma, "Electrical properties of high-quality ultrathin nitride/oxide stack dielectrics," *IEEE Trans. Electron Devices*, vol. 46, pp. 362–368, Feb. 1999.
- [23] V. A. Gritsenko and S. P. Sinitsa, *Silicon Nitride in Electronics*. New York: Elsevier, 1986, pp. 138–237.