2007

TiO2 Breakdown Under Pulsed Conditions

G. Zhao
Old Dominion University

R. P. Joshi
Old Dominion University

V. K. Lakdawala
Old Dominion University, vlakdawa@odu.edu

E. Schamiloglu

H. Hjalmarson

Original Publication Citation

Zhao, G., Joshi, R. P., Lakdawala, V. K., Schamiloglu, E., & Hjalmarson, H. (2007). TiO_2 breakdown under pulsed conditions. *Journal of Applied Physics, 101*(2), 026110. doi:10.1063/1.2425001

TiO_2 breakdown under pulsed conditions

G. Zhao, R. P. Joshi,[a] and V. K. Lakdawala
Department of Electrical and Computer Engineering, Old Dominion University, Norfolk, Virginia 23529

E. Schamiloglu
Department of Electrical Engineering, University of New Mexico, Albuquerque, New Mexico 87131

H. Hjalmarson
Sandia National Laboratories, Albuquerque, New Mexico 87185

(Received 10 July 2006; accepted 2 November 2006; published online 26 January 2007)

Model studies of current conduction and breakdown in TiO_2 were carried out. Our simulation results indicate that electrical breakdown of TiO_2 under multiple-pulsed conditions can occur at lower voltages as compared to quasi-dc biasing. This is in agreement with recent experimental data and is indicative of a cumulative phenomena. We demonstrate that the lower breakdown voltages observed in TiO_2 under pulsed conditions is a direct rise-time effect, coupled with successive detrapping at the grain boundaries. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2425001]

The development of various robust transmission lines with higher energy storage capabilities is an important goal for compact pulsed-power systems. In this context, ceramic dielectrics are emerging as promising candidates from the standpoint of their high dielectric constant and breakdown strength. High dielectric constant (ε) ceramic materials can lead to shorter pulse forming lines, since the length L scales as $(ct_{\text{pulse}})/\varepsilon^{1/2}$. Other advantages include a lower system impedance Z (since $Z \sim \varepsilon^{-1/2}$) and larger energy storage capability.

Though such materials look promising, their breakdown response characteristics have not been well studied nor adequately understood. The breakdown strength of nanocrystalline insulators (e.g., titania) has been observed to increase monotonically with decreases in grain sizes.[1–4] The low conductivity and high hold-off voltage in these materials arise from the presence of fixed charge at grain boundaries that establishes localized Schottky barriers. Samples with smaller average grains present more barriers for a given length and, hence, a larger impediment to conduction. In our experiments, nanocrystalline TiO_2 was seen to exhibit higher breakdown strength as compared to micron sized TiO_2, as shown in Fig. 1.

A second and somewhat surprising observation with regard to high field studies on nanocrystalline TiO_2 has been the *lower breakdown fields under pulsed conditions* as compared to quasi-dc biasing.[5] In these experiments, the "quasi-dc" case consisted of slow ramped voltages (starting from an initial zero value), with increases until device breakdown. The pulsed testing, on the other hand, was performed with a burst of ten pulses per shot until failure. Although only six samples were tested, the results were still able to show a lower breakdown strength under pulsed conditions with some variability,[5] as given in Table I. The energy delivered to the TiO_2 under pulsed conditions is substantially less than that under the dc case. Hence, for such transient pulsing, issues related to possible heating and thermal charge generation can be expected to be weak, and not the probable cause for breakdown. Almost universally, solids have been shown to sustain much higher applied voltages before an eventual breakdown under pulsed conditions as compared to dc biasing.[6] The only reports of higher breakdown fields under dc conditions were observations made on metal semiconductor field effect transistors (MESFETs) containing surface traps.[7,8]

Here we propose a continuum model that includes the presence of internal traps, especially at the grain boundaries. Application of an external electric field works to release electrons from the traps. If sufficiently high electric field magnitudes exist within the TiO_2, then the emitted electrons can undergo impact ionization and contribute to current enhancements. However, if the voltages were driven very slowly, then most of the trapped charge would gradually be emitted and drift out of the device long before the creation of high electric fields. The slow ramped, quasi-dc conditions would then preclude strong charge accumulation and multiplication through internal impact ionization. We hypothesize that the lower breakdown voltages observed in TiO_2 under pulsed conditions is *a direct rise-time effect, coupled with cummulative detrapping*. Under conditions of multiple *short-duration pulsed bursts*, trapped electrons could periodically be released within the device during times of high applied voltages. However, these electrons might not have the requi-

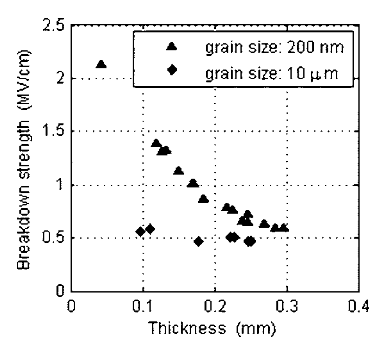

FIG. 1. Breakdown strength vs TiO_2 thickness for nanocrystalline and course-grained materials.

[a]Electronic mail: rjoshi@odu.edu

TABLE I. Breakdown data under dc and Pulsed testing.

Sample number	Sintering temperature (°C)	Thickness (mils)	Breakdown voltage (kV)	Breakdown field (kV/cm)
1	800	6.5	dc: 10	dc: 606
			Pulsed: 4.8	Pulsed: 291
2	800	6.0	dc: 14	dc: 919
			Pulsed: N/A	Pulsed: N/A
3	800	6.0	dc: 7.5	dc: 492
			Pulsed: N/A	Pulsed: N/A
4	850	7.0	dc:18	dc: 1012
			Pulsed: 13.5	Pulsed: 759
5	850	8.5	dc: 16	dc: 741
			Pulsed: 17	Pulsed: 787
6	850	6.0	dc: 11.5	dc: 755
			Pulsed: N/A	Pulsed: N/A

site time nor be subjected to the continued high external fields (due to finite pulse duration) to drive them out of the semiconductor. Hence, cummulative buildup of mobile charge from preceeding pulses would likely occur. Breakdown during a subsequent pulse could then result, as brought out more clearly through our transport simulations.

A one-dimensional (1D), time-dependent simulation based on the continuum, drift-diffusion model of semiconductor transport was applied. A 25 μm TiO_2 ceramic divided into 1000 cells was used with a time step of 10^{-10} s. Six grain boundaries were randomly placed within the simulation region. Holes were neglected, since electrons dominate the electrical behavior[9] of nanocrystalline TiO_2. The basic parameters of this model are listed in Table II and were taken from the literature.[10–14] A trap level located 2.4 eV from the valence band edge with a density of 10^{17} cm^{-3} was assumed.

Standard semiconductor transport equations to include drift and diffusion currents, along with the generation recombination terms, were used.[13,14] Our model included field emission current J, taken to be[13]

$$J = \frac{4\pi q m_n^* k^2}{h^3} T^2 \exp\left(-\frac{q\phi_{B0}}{kT}\right)\exp\left(\frac{q\Delta\phi}{kT}\right)$$
$$= 0.181\,158 \exp\left(\frac{q}{kT}\sqrt{\frac{qE}{4\pi\varepsilon_s}}\right) \ (\mathrm{A/m^2}), \quad (1)$$

and field-dependent drift velocity $v_e(E)$ given by[15]

TABLE II. Parameters used in the simulation model.

Dielectric constant	114[a]
Trap density	$10^{23}/\mathrm{m}^3$[b]
Election effective mass	45 m_0[a]
Electron mobility	0.33 cm^2/V s[c]
TiO_2 electron affinity	3.9 eV[d]
Copper work function	4.7 eV[e]
Free-electron density	$10^{20}/\mathrm{m}^3$
Temperature	300 K
Diffusivity	8.527×10^{-7} m^2 s^{-1}

[a]Reference 6.
[b]Reference 7.
[c]Reference 8.
[d]Reference 9.
[e]Reference 10.

TABLE III. Breakdown voltage and field results for applied ramps.

Ramp slope (V/s)	10^7	10^8	10^9
Breakdown voltage (V)	1569.7	1628	1775
Breakdown field (kV/cm)	628	651	710

$$v_e = \frac{3.3\times10^{-5}E}{[1+(3.3\times10^{-5}E/89)^{1.7}]^{1/1.7}} \ (\mathrm{m/s}). \quad (2)$$

The impact ionization coefficient α for electrons was taken to be

$$\alpha = 9.1\times10^{10}\exp\left(-\frac{7.7\times10^8}{E}\right). \quad (3)$$

Finally, the following expressions were used for electron emission and capture rates from traps:

$$R_{\mathrm{capture}} = 9\times10^{-18}(10^{23}-N_t^-)n, \quad (4)$$

$$R_{\mathrm{emit}} = \frac{N_t^-\exp(1.3\times10^{-4}\sqrt{E})}{4.751\,848}. \quad (5)$$

Based on the above model, simulations were carried out for two different voltage wave forms. One was a linear ramp with a variable slope to mimic the slow turn-on voltage. The other wave forms were rectified sine pulses. The breakdown voltage and the time instant were obtained from the simulation when the device current began increasing without bound. Results for the linear ramp excitation (i.e., quasi-dc), starting from 0 V, are given in Table III. The breakdown times for the 10^7, 10^8, and 10^9 V/s ramped cases were 0.157 ms, 0.016 28 ms, and 1.775 μs, respectively. Clearly, a faster ramp is seen to produce a higher breakdown voltage.

The bias $V(t)$ for rectified sine-wave excitation was taken to be

$$V(t) = \left|A\sin\left(\frac{\pi t}{Ak10^{-9}}\right)\right|. \quad (6)$$

Multiple rectified sine waves were applied until device breakdown. The results obtained are shown in Table IV. The "front" and "tail" in Table IV denote the rising and falling portions of the applied sinusoidal wave form.

The following features become evident from Table IV. (i) As the peak voltage is reduced, there is a greater chance

TABLE IV. Breakdown fields for sine pulses.

Maximum field (kV/cm)	Slope			
	10^9 V/s		2×10^9 V/s	
655	653 kV/cm	First tail	571 kV/cm	First tail
640	639 kV/cm	Second front	636 kV/cm	Fourth tail
636	608 kV/cm	Second tail	611 kV/cm	Sixth tail
632	550 kV/cm	Third tail		
628	628 kV/cm	Sixth tail		

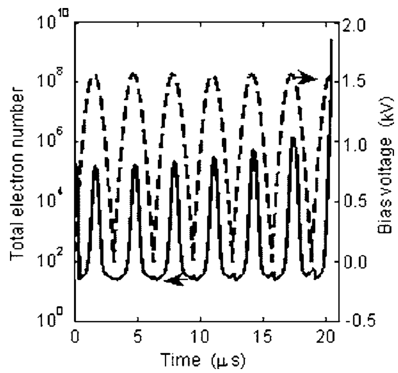

FIG. 2. Time-dependent free-electron density in TiO_2. The applied voltage pulses are also shown for brevity.

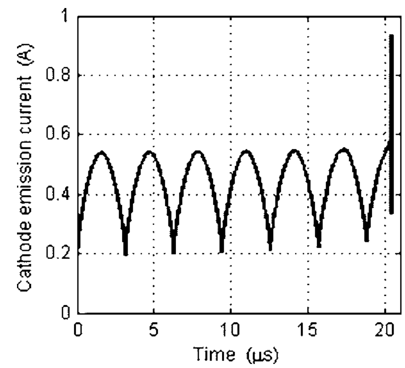

FIG. 3. Time-dependent cathode emission current corresponding to the voltage pulses of Fig. 2.

that breakdown occurs later in time and requires more pulses. For example, the 655 kV/cm case is predicted to break down within the first pulse, while the reduced 628 kV/cm bias requires six pulses before breakdown. (ii) A cumulative memory effect is thus manifested in the device response. (iii) For a slower rise in voltage [i.e., a higher k value in Eq. (6)], the breakdown voltage decreases and more pulses are required, all other parameters being fixed. This is again indicative of finite time requirements for the inherent processes leading to final breakdown. (iv) Under a multiple-pulse bias, the breakdown voltage changes rapidly with the pulse peak value. Small changes in the peak value are seen to lead to a big change in breakdown voltage. Hence, multipulse breakdown voltages cannot be used as a unique measure of the insulation strength. (v) In comparison to quasi-dc excitation, *lower breakdown voltages can result* under multiple pulsing. This is in agreement with the experimental data of Table I. For example, breakdown voltages of 1569.7 and 1775 V are predicted for the 10^7 and 10^9 V/s ramps. However, a much lower threshold of 1374.1 V results for the sinusoidal pulsed excitation.

The cumulative effect can be seen more clearly from the time-dependent free-electron population during different pulses, shown in Fig. 2. The applied voltage pulses are also included for brevity. The maximum bias was 1570 V and corresponds to the last row of Table IV. The gradual and progressive rise in free-carrier density (on a "semilog" scale) is obvious. Essentially, in this multiple short-duration pulsed-burst scenario, trapped electrons are periodically released within the device upon voltage application. These electrons do not have the requisite time, nor are they subjected to the continued high fields necessary for driving them out of the semiconductor. This, in turn, progressively enhances the electron production through impact ionization as the "base line electron population" increases. Eventually an electron driven avalanche breakdown occurs.

The cathode emission current in the TiO_2 device shows negligible cumulative effects, as illustrated in Fig. 3. This implies that the breakdown is mainly due to bulk impact ionization, and not through cathode emission. The simulations also indicated that breakdown was initiated from the cathode end. The electron density at the cathode end (not shown) was almost 1000 times larger than that at the central part, and a high electric field magnitude of $\sim 1.2 \times 10^8$ V/m at the cathode surface was predicted. The movement of avalanching electrons to the anode left a net positive charge close to the cathode and worked to enhance the local field.

In summary, numerical studies of current conduction and breakdown in TiO_2 were carried out. Our results indicate that electrical breakdown of TiO_2 under multiple-pulsed conditions can occur at lower voltages as compared to quasi-dc biasing, in agreement with experiments. Also, the multipulse breakdown voltage has been shown to dramatically depend on the peak value of the applied pulse. We hypothesize that the lower breakdown voltages under pulsed conditions is a direct consequence of occupied traps, especially at the grain boundaries of such nanocrystalline material. Thus, the increased hold-off voltage with denser granularity is attained, but at the price of lower device reliability and lifetime.

This work was sponsored in part by AFOSR and Sandia National Laboratories. Useful discussions with M. Kristiansen (TTU) and R. Curry (U. Missouri) are gratefully acknowledged.

[1] G. D. Mahan, L. M. Levinson, and H. R. Philipp, J. Appl. Phys. **50**, 2799 (1979); M. Bartkowiak and G. D. Mahan, Phys. Rev. B **51**, 10825 (1995).
[2] R. P. Joshi and R. F. Wood, J. Appl. Phys. **84**, 3197 (1998).
[3] S. Li, J. Li, F. Liu, M. A. Alim, and G. Chen, J. Phys. D **35**, 1884 (2002).
[4] P. Castro, J. Buchenauer, J. Gaudet, and E. Schamiloglu, Digest of Technical Papers, IEEE Catalog Number 05CH37688C, Proceedings of the 15th IEEE Pulsed Power Conference, Monterey, CA, 2005, pp. 978–981.
[5] C. L. Li, T. M. Barton, and R. E. Miles, IEEE Trans. Electron Devices **40**, 811 (1993).
[6] T. M. Barton, C. M. Snowden, J. R. Richardson, and P. H. Ladbrooke, Electron. Lett. **23**, 686 (1987).
[7] J. Nelson, Phys. Rev. B **59**, 15374 (1999).
[8] F. A. Grant, Rev. Mod. Phys. **31**, 646 (1959).
[9] P. E. de Jongh and D. Vanmaekelbergh, Phys. Rev. Lett. **77**, 3427 (1996).
[10] R. G. Breckenridge and W. R. Hosler, Phys. Rev. **91**, 793 (1953).
[11] R. Konenkamp, Phys. Rev. B **61**, 11057 (2000).
[12] P. A. Montano and G. W. Fernando, Phys. Rev. Lett. **59**, 1041 (1987).
[13] For example, S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley, New York, 1981).
[14] R. B. Darling, J. Appl. Phys. **74**, 4571 (1993).
[15] I. A. Khan and J. A. Cooper, Jr., IEEE Trans. Electron Devices **47**, 269 (2000).