A Sensitivity Map-Based Approach to Profile Defects in MIM Capacitors From IV-CV-GV Measurements

Andrea Padovani, *Member, IEEE*, Ben Kaczer, Milan Pešić, *Member, IEEE*, Attilio Belmonte, Mihaela Popovici, Laura Nyns, Dimitri Linten, Valeri V. Afanas'ev, Ilya Shlyakhov, Younggon Lee, Hokyung Park, Luca Larcher

Abstract— We present a defect spectroscopy technique to profile the energy and spatial distribution of defects within a material stack from leakage current (J-V), capacitance (C-V) and conductance (G-V) measurements. The technique relies on the concept of sensitivity maps (SM), that identify the band-gap regions where defects affect those electrical characteristics. The information provided by SMs are used to reproduce J-V, C-V and G-V data measured at different temperatures and frequencies by means of physics-based simulations relying on an accurate description of carriers-defect interactions.

The proposed defect spectroscopy technique is applied to ZrO₂-based metal-insulator-metal structures of different composition for DRAM capacitor applications. The origin of the observed voltage, temperature and frequency dependencies of the I-V, C-V and G-V data is understood and the atomic structure of the relevant stack defects is identified.

Index Terms— DRAM, ZrO₂, Defect Spectroscopy, Metal-Insulator-Metal capacitor, gate leakage, capacitance, conductance.

I. INTRODUCTION

DYNAMIC Random Access Memories (DRAM) are a key element of modern computing systems and applications. Even though there is a significant research effort invested in the novel material systems i.e. STO-based [Schmelzer14, Pesic16], physical thickness of these dielectrics, required to reach sub 10⁻⁷ [A/cm²] leakage, excides the sub-20 nm node requirements. Existing, state-of-the-art DRAM is based on ZrO₂/Al₂O₃/ZrO₂ (ZAZ) film stack and still those films are

considered as the most promising candidates [Kil06], [Martin13], [Pesic16], [Onaya16], [Lee17] as the basis of the sub-20nm DRAM nodes. These films also gained additional attention in 2016 when Pešić et al. [PesicAdv.Fun.Mat16] reported the anti-ferroelectric-like (AFE) behavior in both ZrO₂ and ZAZ stack as well as suggested not only how the non-volatility can be induced in those ZrO₂-based DRAM films [Pesic IEDM16] but also how the equivalent can be used as the tunnel junctions in X-point memories [PesicJEDS18].

In this paper we will focus on the material and defect characterization using a defect spectroscopy technique based on the accurate modeling and simulation of the carrier-defects interactions. Dielectric defects are the basis of the most relevant reliability phenomena in both logic and memory devices such as Bias Temperature Instabilities (BTI), Random Telegraph Noise (RTN), Stress Induced Leakage Currents (SILC) and breakdown (BD). For the specific case of DRAM technology, the presence of defects in the dielectric stack is expected to originate nonlinear C-V characteristics and leakage currents, both detrimental for device reliability [Kaczer13]. Identifying their nature and their spatial/energy distribution within the capacitor stack is thus crucial for process optimization, reliability improvement and cell scaling. The power of the defect spectroscopy will be demonstrated on ability to predict a fast current (dielectric transients) transient. To this aim the paper is organized as follows: In Section II a fabrication detail and experimental methods are disclosed. In next, section III defect spectroscopy technique is presented. This is followed with results and discussion after which paper is concluded.

II. DEVICES AND MATERIAL CHARACTERISTICS

The four ZrO₂-based MIM capacitor structures considered in this work are shown in Fig. 1, top row. Two of them, D02 and D03, consist of a single ZrO₂ layer, whereas the other two, D04 and D05, comprise a 0.5nm-thin Al₂O₃ layer sandwiched between two ZrO₂ layers to form a ZrO₂/Al₂O₃/ZrO₂ (ZAZ) stack.

The ZrO₂ films were deposited by atomic layer deposition (ALD) using TEMAZ (Tetrakis(ethylmethyldamido)zirconium) as Zr precursor and H₂O as oxidant at a temperature of 250 °C. The nominal thicknesses were 4 nm (D02, D06) and 8 nm (D03-D05, D07-D09) ZrO₂. A 0.5 nm Al₂O₃ layer was deposited at 300 °C on top of D04, D05, D08 and D09. The

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A. Padovani is with MDLSoft Inc., 5201 Great America Parkway, Suite 320, Santa Clara, CA 95054, USA (e-mail: andrea.padovani@mdlsoft.com).

S. B. Author, Jr., was with Rice University, Houston, TX 77005 USA. He is now with the Department of Physics, Colorado State University, Fort Collins, CO 80523 USA (e-mail: author@lamar.colostate.edu).

T. C. Author is with the Electrical Engineering Department, University of Colorado, Boulder, CO 80309 USA, on leave from the National Research Institute for Metals, Tsukuba, Japan (e-mail: author@nrim.go.jp).

Fig. 1. Schematic representation of the ZrO₂-based MIM and MIS capacitors considered in this work.

Fig. 2. (a) Schematic representation of the band diagram considered for the D06-D09 structures indicating the quantities used for the calculation of Φ_M . (b) estimation of the EFW.

dielectric stack deposition was completed with a 2 nm ZrO₂ (D04, D08) or 3 nm ZrO₂ (D05, D09). These dielectric stack combinations are atop of a 10nm-thick TiN bottom electrode (BE). The MIM stack is completed by the deposition of the 30nm-thick TiN top electrode (TE). The films crystallized after post-deposition anneal at 500 °C in N₂ for 3 min (D02-D09).

To extract the TE effective work function (EFW), four corresponding stacks were fabricated with a Silicon BE and slanted SiO₂ oxide in a Metal-Insulator-Semiconductor (MIS) configuration (D06-D09 in Fig. 1, bottom row).

Electrical characterization was carried out using a semiautomatic probe station equipped with a Keithley 2636 current/voltage and Keysight E4980 precision LCR meters. Fast transient current relaxation measurement was carried out using a custom-made instrument [refReisinger]. This instrument applies a charging pulse of amplitude V_{charge} and duration t_{charge} to the measured capacitor and then shorts it or 0.75 us. The build-up of voltage on the capacitor is then monitored as a function of time over multiple decades (~1 us – 1 s) and can be further converted to charge loss or $J_{relax}(t)$.

Extraction of the EFW (Φ_M) and of the barrier at the electrode/oxide interfaces (Φ_b) is important for correctly constructing the device band structure and in turn accurately profiling the defect distribution. The effective electrode work function Φ_M was extracted from flat-band voltage (V_{FB}) measurements on the MIS structures D06-D09 while assuming the band configuration in Fig. 2(a). $E_C - E_F$ is assumed to be 0.99 eV, corresponding to $N_A = 2 \times 10^{17} \text{ cm}^{-3}$ as extracted from the fit of CVs taken at 10 kHz (not shown), X_{Si} is 4.05 eV. The V_{FB} is extracted from a CV characteristic using the Hauser technique [Hauser] and then used to calculate the work function as $\Phi_M = X_{Si} + (E_C - E_F) - V_{FB}$. The extrapolated values for the four MIS wafers D06-D09 are shown in Fig.

Fig. 3. IPE spectra collected at negative and positive bias voltages on samples (a)-(b) D03 and (c)-(d) D05. (e)-(f) Thresholds Φ extracted from the IPE spectra shown in panels (a)-(d) are plotted as a function of the oxide electric field using Schottky plots $\Phi-(F)^{1/2}$.

TABLE I
ESTIMATED TE AND BE BARRIER HEIGHTS

Sample	TE Φ_b (eV) ($V_G < 0V$)	BE Φ_b (eV) ($V_G > 0V$)
D03	~ 2.3	~ 2.3
D04	~ 2.1	~ 2.2
D05	~ 2.4	~ 2.4

2(b). Best fit to the EWF vs. high-k EOT dependence across all four wafers is achieved considering a SiO₂/high-k interface charge $\rho_i = 4 \cdot 10^{12} \text{ cm}^{-2}$ and a high-k bulk charge $\rho_{HK} = 5.5 \cdot 10^{18} \text{ cm}^{-3}$. The EWF Φ_M is estimated to be $\sim 5.0 \pm 0.1 \text{ eV}$.

Internal Photoemission (IPE) is then used to estimate the barrier at the electrode/oxide interfaces. Provided the electrode is thin enough, intensive monochromatic light with energy $h\nu$ can be used to excite carriers from either the TE or the BE. Electrons with enough energy $h\nu$ can surpass the barrier Φ_b and be injected into the oxide conduction band, to be detected as an additional current by the measurement circuit. Typical accuracy of the IPE technique to determine Φ_b is $\pm 0.1 \text{ eV}$ taking into account the field-dependent barrier height caused to image-force interaction of an electron with a polarizable photoemitter [Afanas'ev07]. IPE spectra collected on MIM samples D03 and D05 are shown respectively in Figs. 3(a)-(b) and 3(c)-(d) for opposite bias polarities on TE corresponding to electron emission from the TE (negative bias) and BE (positive bias). The extracted thresholds Φ are then plotted as a function of the oxide electric field (F) and extrapolated to zero electric field using Schottky plots $\Phi-(F)^{1/2}$ shown in Fig. 3(e)-(f). As a reference, the expected in an ideal case barrier lowering with the image force dielectric constant $\epsilon_i \approx 5$ ($\epsilon_i \approx n^2$, where $n=2.2$ is the refractive index of ZrO₂ determined from spectroscopic ellipsometry measurements) is shown with a dashed line. This ideal case corresponds to a uniform, charge-free interface.

Fig. 4. Capacitance-voltage characterization of (a) D03 and (b) D05. Symbols: Single C-V measurements, the subsets of which were used for defect profiling. Lines: Hysteretic loops measured by increasing the maximum voltage $|V_{MAX}|$ (from 0.5V to 3V for D03 and from 1.5V to 4V for D05) with 0.5V steps. Numbers indicate the measurement order. Hysteretic measurements are offset each by 1.5 mCm⁻² for clarity.

Much larger than expected barrier lowering corresponding to unrealistically lower ε_i suggests the formation of laterally non-uniform interface barrier [Ref= V. V. Afanas'ev, N. Kolomiets, M. Houssa, and A. Stesmans, Internal Photoemission Metrology of Inhomogeneous Interface Barriers, *Phys. Status Solidi A* **215**, 1700865 (1-12) (2018)] Values in the range of 2.1eV-2.4eV are consistently extracted for TE and BE barrier heights for all the measured samples, as reported in Table I which corresponds to the range of the metal workfunction differences found for TiN grains of different crystallographic orientation [Bolotov 2015].

Leakage current density characteristics (J-V) were measured on MIM capacitors D02-D05 at different temperatures (0, 25, 50, 75, and 100°C) on multiple samples and areas to guarantee data uniformity and to exclude perimeter leakage. Delay of 1 s between every voltage step and current measurement was used to suppress relaxation processes.

As expected from [ref], the equivalent material system investigated in this study also exhibited Antiferroelectric (AFE)-like behavior, characterized by a double butterfly capacitance-voltage (C-V) curve [see Fig. 4(a)-(b)]. As AFE are known to its volatile behavior and the fact that the gain generated with the AFE switching is relaxed with removal of the external excitation, we carried out C-V experiment in an incrementing manner to rule-out the impact of the AFE relaxations on the defect characterization. Voltage was swept

from 0 to $|V_{MAX}|$ and back to capture the turning when the AFE-switching and ionic processes start impacting the C-V characteristics. Results shown in Fig. 4 indicate that up to 2V-2.5V there is no hysteretic behavior originating from AFE switching [cf. traces 2 and 4 in Figs. 4(a) and (b)].

Finally, capacitance-voltage (C-V) and conductance-voltage (G-V) characteristics were taken in frequency range of 500 Hz – 2 MHz and the temperature range 0 – 100 °C. Smallest accessible capacitors (53x53 μm^2) were used to minimize the impact of series resistance at higher frequencies and all data affected were excluded from further analysis. The voltage range was limited to below AFE polarization switching (cf. Fig. 4).

III. THE DEFECT SPECTROSCOPY TECHNIQUE

The fast defect spectroscopy technique we developed is based on the accurate modeling and simulation of the carrier-defect interactions that are at the bases of defect-assisted trapping and transport [Vandelli11]. Simulations are performed with the Ginestra™ software [Ginestra], a multi-scale simulation platform that self-consistently describes all the mechanisms relevant for dielectric stacks used in logic [Vandelli11], [Padovani13], [Vandelli14], [Padovani17-2], and memory devices (Resistive RAMs [Padovani16], ferroelectric [Pesci18], etc.). This includes defect-assisted charge trapping and transport, described in the framework of the multi-phonon theory accounting for carriers-phonons coupling and lattice relaxation processes [Huang50], [Henry77], [Vandelli11], [Zhang11], current-induced power dissipation and temperature increase, distortion and breakage of atomic bonds promoted by field, temperature and electron injection [Padovani17-2], diffusion of atomic species [Padovani16] and ferroelectric switching [Pesci18]. Calculations are performed considering the local potential given by the applied bias and the defect charge state and occupation. Non-defect-related conduction mechanisms such as direct/Fowler-Nordheim tunneling, thermionic emission, and drift are also considered consistently with Trap-Assisted-Tunneling (TAT), which is the dominant transport mechanism in a wide variety of dielectric materials [Vandelli11], [Nasyrov11], [Jegert11], [Padovani13-2].

The accurate physical framework provided by Ginestra™ is exploited by the developed spectroscopy technique in a two-step procedure. The first step is the derivation of the Sensitivity Map (SM), a theoretical construct identifying dielectric regions (in both energy and space) where defects mostly affect a specific electrical characteristic [Sereni16], [Padovani17]. To this purpose, the contribution of the defects is evaluated with respect to all their possible energy-space (E, z) positions in the device band-gap. The desired electrical quantity (gate current, capacitance or conductance) is then calculated for every considered (E, z) position and normalized with respect to its maximum value. The SM is finally obtained by identifying the regions where the normalized quantity is above a given threshold (e.g. 5-10% for the I-V and 90-95% for the C-V/G-V), corresponding to the portions of the band-gap where the defects mostly affect the considered electrical characteristic [Sereni16]. It must be noted that trap-to-trap transitions are neglected in the calculation of the SMs,

Fig. 5. Gate Current sensitivity map calculated at different gate voltages for the 8nm-thick ZrO_2 MIM D03. The sensitivity region represents the (E, z) coordinates where the normalized current is equal or above to 5% of the maximum value.

Fig. 6. Capacitance sensitivity map calculated at different gate voltages and frequencies for the 8nm-thick ZrO_2 MIM D03. The sensitivity region represents the (E, z) coordinates where the normalized current is equal or above to 90% of the maximum value.

although they are expected to be important for the gate leakage current, especially in the case of thicker oxides (on the contrary, their impact on C-V and G-V is negligible). Nevertheless, as will be discussed below, SMs are used as input for the subsequent electrical characteristics simulations in which trap-to-trap transitions are properly considered. The SMs depend on voltage, temperature and material/defect parameters such as the relaxation energy. They are also measurement-specific, as different electrical tests are typically sensitive to defects located in different portions of the band-gap. The gate current SMs calculated at $V_G = -2\text{V}, -1\text{V}, 1\text{V}$ and 2V for sample D03 are shown in Fig. 5. Results clearly show that the gate leakage current is mostly sensitive to the defects located in the central portion of the dielectric, since they are the ones minimizing the average tunneling distance [Sereni16]. The C-V sensitivity maps calculated for the same stack at the frequencies of 100Hz and 1MHz are shown in Fig. 6. Differently from the case of the I-V, the defects mostly contributing to the capacitance are located close to the interfaces: the higher (lower) the AC signal frequency, the closer (further away) to the interface the defects that contribute to the capacitance. The results shown in Figs. 5 and 6 suggest that the combination of I-V and C-V sensitivity maps allows obtaining information on the whole band-gap.

Figure 7 shows a schematic representation of the frequency

Fig. 7. Schematic illustration on the τ_c/τ_e plot of the oxide traps responding to the AC signal applied during C-V/G-V measurements (blue ellipses) as a function of frequency and temperature.

and the temperature response of oxide traps during C-V and G-V measurements. When a small AC signal with frequency f is applied on top of the DC bias during such measurement, only the oxide traps with capture time τ_c comparable to emission time τ_e (blue ellipses in Fig. 7) will contribute to the AC current measured by the LCR meter. When f is increased, a smaller fraction of traps will respond, since their τ_c and τ_e will be above $\sim f^{-1}$. In contrast, increased temperature T results in lower τ_c and τ_e and thus to a larger trap contribution to capacitance, Fig. 7(b).

The second step of the defect spectroscopy technique consists in the use of the calculated sensitivity maps as inputs to identify the actual defect distributions allowing reproducing the measured electrical data [Sereni16], [Padovani17]. The defect density distributions are designed according to the sensitivity maps calculated at different voltages and/or temperatures and their accuracy is verified by evaluating the agreement between simulations and measurements. A fine tuning is performed to adjust the distribution properties, especially the defect density, to accurately reproduce the experimental characteristics. At the end of the procedure, the defect spectroscopy provides the (E, z) map of the defects that are responsible of the observed voltage, temperature and frequency dependence of the experimental data. It also provides the defects relaxation energy (E_{REL} , estimated from the temperature dependence), a fundamental parameter representing the energy that is required for the lattice relaxation process to occur [Huang50], [Henry77], [Vandelli11], [Zhang11] and that determines capture and emission time constants as well as their temperature dependence. More importantly, E_{REL} is directly linked to the atomic structure of the defects and can thus be used, together with the defects thermal ionization energy band, to identify the physical nature of the defects assisting the TAT transport and responsible for the C-V/G-V frequency dispersion [Vandelli11].

IV. RESULTS AND DISCUSSION

The defect spectroscopy technique described in the previous Section has been applied to the MIM samples in Fig. 1 to identify and profile (in energy and space) the defects responsible for the voltage, temperature and frequency dependence of the measured data. Table II reports the material parameters considered in the DS simulations. Note that the values of ZrO_2 dielectric constant, TiN metal work-function and BE/TE barrier height (given by $WF_{\text{TiN}} - \chi_{\text{ZrO}_2}$) are the

Fig. 8. Gate current as a function of temperature, capacitance and conductance as a function of frequencies ($T=50^\circ\text{C}$) measured (symbols) and simulated (lines) on samples (a)-(c) D03, (e)-(g) D04 and (i)-(k) D05. (d), (h), (l) Energy and space distribution of the stack defects as extracted by using the defect spectroscopy to reproduce the data in (a)-(c), (e)-(g) and (i)-(k).

ones derived from the experimental characterization discussed in Section II. The DS results are summarized in Fig. 8 for samples D03, D04 and D05 (from left to right), where the simulated electrical characteristics are compared with the experimental data. As can be seen C-V and G-V exhibit a non-linear and asymmetric behavior independently on the stack composition, which suggests a common origin of both frequency and voltage dependencies. Moreover, leakage affects the conductance at higher voltages for the case of the thinner sample, see Fig. 8(c). The I-V, C-V and G-V characteristics of every sample are nicely (and simultaneously) reproduced in the whole voltage, temperature and frequency

range considered. The corresponding energy and space distribution of the stack defects extracted using the DS are shown in Figs. 8(d), (h) and (l). They highlight the presence of a defect band located between 1.1 eV and 3.3 eV below the ZrO_2 conduction band minimum. The distribution is slightly shallower in the bulk of the material and gets deeper and narrower close to the electrodes, mainly because of the reduced energy resolution provided in that region by CV measurements (see Fig. 6). The extracted energy range is consistent with the levels calculated for oxygen vacancies in ZrO_2 [Foster02], [Perevalov17]. A higher defect density (up to $2 \times 10^{21} \text{ cm}^{-3} \text{ eV}^{-1}$) is extracted close to electrode/oxide

TABLE II
MATERIAL PARAMETERS CONSIDERED IN DS SIMULATIONS

Quantity	Value
ZrO ₂ relative dielectric constant (κ_{ZrO_2})	33
ZrO ₂ electron affinity (χ_{ZrO_2})	2.55eV
ZrO ₂ band-gap ($E_{\text{G,ZrO}_2}$)	5.8eV
ZrO ₂ tunneling effective mass (m_{ZrO_2})	0.35 m_0
Al ₂ O ₃ relative dielectric constant ($\kappa_{\text{Al}_2\text{O}_3}$)	11
Al ₂ O ₃ electron affinity ($\chi_{\text{Al}_2\text{O}_3}$)	1.45eV
Al ₂ O ₃ band-gap ($E_{\text{G,Al}_2\text{O}_3}$)	8.8eV
Al ₂ O ₃ tunneling effective mass ($m_{\text{Al}_2\text{O}_3}$)	0.2 m_0
TiN work function (WF_{TiN})	4.9eV

Fig. 9. Voltage-dependent exponent n in $C \sim f^{n-1}$ calculated from C-V-f data in the 2kHz-12.6kHz frequency range at 50°C (lines) well matches measurements on samples D03 and D05 (symbols).

interfaces and is responsible for the U-shaped capacitance vs. voltage characteristics. The V_G asymmetry observed across all samples in both CV and GV data (i.e., the higher capacitance and the conductance ‘humps’ at positive gate voltages) is reflected by the larger concentration of defects spatially located close to the bottom electrode and with an energy above the metal Fermi level, consistently extracted for all MIM samples. A high defect density is observed also in the thin AlO and in the nearby portions of the adjacent ZrO₂ layers of samples D04 and D05, probably indicating a strong interaction (and intermixing) of the two materials. Conversely, a lower defect density (in the range of 10^{19} - 10^{20} cm⁻³eV⁻¹) is found in the ZrO₂ bulk.

The results in Fig. 8 clearly indicate that the extracted defect populations are at the origin of the capacitance/conductance frequency dispersion. Other phenomena such as dielectric relaxation (DR) – related to the inability of the polarization processes to follow the rate of change of an applied oscillating electric field [DielRelBook] – are expected to not play a role. This because the main *intrinsic* polarization mechanisms (the so-called electronic, atomic and orientational polarization [DielRelBook]) have characteristic frequencies in the range of 10^7 - 10^{15} Hz, much higher than the considered measurement range.

Figure 9 further documents that when the C-V frequency dependence is described $C \sim f^{n-1}$ (Curie-von Schweidler law), the extracted voltage-dependent exponent n is fully reproduced by our simulations assuming only the extracted

Fig. 10. Comparison between relaxation currents measured (symbols) and simulated (lines) on device D03 after a charging pulse ($t_{\text{charge}}=64\text{ms}$; $V_{\text{charge}}=0.25\text{V}/0.5\text{V}/0.75\text{V}/1\text{V}$). Simulations have been performed considering the defect distribution extracted using defect spectroscopy as in Fig. 8(d). The applied pulse is shown in the inset.

trap distributions.

To further understand the possible role of DR, we used the extracted defect distributions to simulate the trap contribution in typical dielectric relaxation experiments [Xu04]. These experiments represent a figure of merit of DRAM capacitors and have been previously attributed to polarization relaxation of the dielectric material [Reisinger01], [Jameson03] or to charge trapping/de-trapping effects [Bachhofer01], [Dumin93]. Figure 10 shows the results of the DR measurement, carried out on device D03, together with a schematic representation of the applied pulse sequences. As can be seen, simulations performed considering the device extracted with the defect spectroscopy [Fig. 8(d)] reproduce nicely the measured data. Note that similar results cannot be achieved when a defect distribution significantly different from the one in Fig. 8(d) is considered (not shown). On one hand, this clearly demonstrates the key role played by the defects in these relaxation processes. In addition, the results shown in Fig. 9 confirm the power and capabilities of the proposed DS technique in predicting device reliability characteristics, even the complex ones the DR is.

The defect spectroscopy also provides an estimation of the relaxation energy, a parameter that is directly linked to the atomic structure of the defects and can thus be used to identify their physical nature by comparison with the values provided by ab-initio calculations. Table III summarizes the values of E_{REL} extracted by applying the DS to samples D03, D04 and D05 and the ones calculated in [Perevalov17] for 4- and 3-fold coordinated (4f and 3f) oxygen vacancies (VO) with different charge states (positive, V^+ , neutral, V^0 and negative, V^-) in monoclinic ZrO₂. The relaxation energy of ZrO₂ defects extracted for the different samples is distributed in the 0.9eV-1.3eV and agrees well with the values calculated for 3f- and 4f- positively charged VO [Perevalov17]. This indicates that the charge trapping and transport phenomena in the considered ZrO-based stacks are assisted by V^+ defect configuration ($V^+ + e^- \rightarrow V^0 \rightarrow V^+ + e^-$), providing key information for process optimization.

TABLE III. THERMAL IONIZATION (E_T) AND RELAXATION (E_{REL}) ENERGY VALUES (IN eV) OF ZrO_2 DEFECTS AS OBTAINED FROM DEFECT SPECTROSCOPY AND AB-INITIO CALCULATIONS

Defect Spectroscopy				Ab-Initio Calculations [Perevalov17]					
	D03	D04	D05	V ⁺ (3f)	V ⁰ (3f)	V ⁻ (3f)	V ⁺ (4f)	V ⁰ (4f)	V ⁻ (4f)
E _T	between 1.1 and 3.3			1.25	1.15	0.16	1.45	1.5	0.33
E _{REL}	0.93	1.22	1.2	0.82	0.56	0.09	1.03	0.65	0.28

V. CONCLUSIONS

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