Research paper

Defect correlated with positive charge trapping in functional HfO₂ layers on (100)Si revealed by electron spin resonance: Evidence for oxygen vacancy?

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article info abstract

Article history:

Received 24 February 2017

Received in revised form 25 April 2017

Accepted 27 April 2017

Available online 03 May 2017

We report on the results of low-temperature K- and Q-band electron spin resonance (ESR) measurements on three types of device-grade HfO₂ films deposited on p-(100)Si by chemical vapor deposition (CVD) using different precursors. The study has been carried out in combination with ex situ contactless charge injection, complemented with various post-growth irradiation treatments, with the intent to assess the presence and atomic nature of occurring charge trapping centers. In HfO₂ layers grown by atomic layer (AL) and metal-organic (MO) CVD, this reveals the reproducible appearance of a paramagnetic center, termed H5, in firm correlation with alternate positive/negative charge injection, i.e., distinct signal intensity increase/decrease, respectively. Simulation of the observed powder pattern for both K- and Q-band consistently points to a defect of orthorhombic symmetry characterized by $g_1=1.880\pm0.006$, $g_2=1.900\pm0.006$, $g_3=1.981\pm0.0015$. Analysis based on the inferred spectroscopic ESR characteristics in comparison with previous theoretical work leads to the suggestion that the observed center may concern an O-vacancy defect, closest perhaps to the 4-fold 1+charged O-vacancy (V_{O4}

+). The revealed defect may account, at least partly, for the previously reported distinct propensity of positive charge trapping in Si/hafnia structures grown by ALCVD and MOCVD.

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Keywords:

High-k dielectric

Si/hafnia structure

Charge trapping

Oxygen vacancy

ESR

1. Introduction

Over the last decade, the conventional SiO_x(N_y) gate dielectric in Sibased complementary metal-oxide-semiconductor integrated circuits has been replaced by Hf-oxide based insulators of high dielectric constant κ . The transition has been forced in order to meet the required reduction in equivalent oxide thickness of the gate dielectric as device scaling advances relentlessly. In taking such drastic step, stringent requirements must be met, a crucial one being that the replacing oxide must be low on defect (trap) density. The latter appeared critical for oxides such as HfO₂ and ZrO₂, suffering, among others [1–4], from intolerable charge trapping. Various oxide-defect related detrimental effects have been reported, such as severe reliability issues associated with charge trapping in metal-HfO₂-Si transistors [5,6] and degradation of retention and endurance of flash cells [7].

Oxygen vacancies, deemed as dominating intrinsic defects in the bulk of transition metal oxide films, are generally advanced as the culprit for any degradation related with the HfO₂ dielectric [1,8]. O-vacancy defects have been associated with electron traps with energy levels in the range 1.2–1.8 eV below the oxide conduction band edge [5,7]. Yet, recent work has demonstrated two kinds of deep electron traps in HfO₂ films which would not implicate O vacancies [9]. Pertinently, as properly outlined by Xiong et al. [10] and consolidated later [3,4,11–14], theoretical work has concluded that the O vacancy in HfO₂ has five possible charge states and can also act as hole trap [3,4,10–14]; An optimized scheme of the localization of the corresponding energy levels in the HfO₂ band gap has been presented by Ramo et al., [3,4] and has been addressed in various other works as well [10,11,14].

Yet, different from their commonplace “culprit” status, oxygen vacancies have also been allotted benign influences as being at the origin of more intriguing physical effects in hafnia. One work reported on the observation of ‘highly-doped’ semiconducting behavior of oxygen-deficient HfO_{2-x} thin films grown by controlled-oxygen reactive molecular beam epitaxy, tentatively ascribed to the formation of a vacancy-induced p-type dopant defect band [15]. Additionally, other work reported on the observation of unexpected ferromagnetism in thin HfO₂ films [16], which was attributed to oxygen vacancies –an assignment that

was later countered, ascribing the observed ferromagnetic behavior as rather originating from transition metal impurities [17,18]. Along these lines, as stated before [4], oxygen vacancies are considered as dominating intrinsic imperfections in the bulk of various transition metal oxides, such as HfO_2 and ZrO_2 , and are thought to be present in high densities as well in thin films. However, conclusive chemical demonstration of the O vacancy, as might, e.g., be provided by electron spin resonance (ESR), is still pending. Rather recent theoretical work [13] has tentatively assigned an ESR signal observed in m- HfO_2 powders [19], termed H1 and of axial symmetry ($g_{\parallel}=1.938\text{--}1.941$; $g_{\perp}=1.970$), to the 1+charged 3-fold O-vacancy, $\text{V}_{\text{O}3}$

+. Though inconsistent with the calculated manifest orthorhombic symmetry, the reasoning was upheld by considering two calculated principal g values (g_1, g_2) as quite close, leaving some inconclusiveness. Moreover, direct experimental chemical evidence for the O vacancy being involved in charge trapping appears so far elusive.

Here, aiming to provide direct insight, we report on a first ESR observation in functional hafnia layers on Si of a paramagnetic point defect showing manifest correlation with positive charge trapping. Its potential origin as a basic oxygen vacancy is analyzed.

2. Experimental

Three types of HfO_2 (100–110 nm thick) films, in the polycrystalline/amorphous state, were deposited on p-type (100)Si ($\sim 800\ \mu\text{m}$ thick) via different chemical vapor deposition (CVD) procedures [20]: (1) Atomic layer (AL) CVD at 300 °C using HfCl_4 and H_2O as precursors at a pressure of ~ 1 Torr; (2) metallo-organic (MO) CVD at 485 °C from tetrakisdiethylaminohafnium ($\text{C}_{16}\text{H}_{40}\text{HfN}_4$) and O_2 precursors. The Imec predeposition surface cleaning is applied in both cases, followed by growing of a thin Si oxide in ozonated water to improve HfO_2 nucleation; (3) NCVD from the $\text{Hf}(\text{NO}_3)_3$ precursor on HF-last (100)Si surfaces at 350 °C, i.e., in nominally H and C free conditions, unlike the two previous methods.

To assess the possible correlation of charge trapping with ESR spectral responses, as searched for, the dielectric HfO_2 layers were subjected to post-deposition (PO) charge injection using the corona ion technique. As mere advantage, this represents a contactless charging method, thus eliminating the need for conductive electrode deposition that would invariably impede ESR observations. Both positive and negative corona charge injection was applied, but for times kept very short (~ 10 s) to avoid as much as possible irreversible (structural) sample degradation inherent to the technique [21]. The impact of charge injection was probed by ESR typically within a time span ≤ 1 h after finishing the corona treatment. After initial ESR tests, to reveal defects, additionally applied were ex situ unbiased irradiation by UV, vacuum UV (10 eV; $\sim 3 \times 10^{15}$ photons cm^{-2} s $^{-1}$), or ^{60}Co γ photons to a dose of 50 Mrad(Si). Some samples were subjected to PD anneal in N_2 (1 atm; ~ 30 min) in the range 300–900 °C.

Both conventional 1st harmonic and high power 2nd harmonic phase quadrature K and Q-band ESR observations were carried out in the temperature range $T = 4.2\text{--}30$ K, usually with the direction of applied magnetic field B parallel to the (100)Si/ HfO_2 interface normal n .

But to check ESR signal anisotropy, additional control field angular dependent measurements were made for B , at angle ϕ_B with n , rotating in the (110)Si substrate plane. As demonstrated before empirically, under appropriate spectroscopic conditions for a specific type of defect, the second ESR detection mode may favorably be used as the detected signals appear identical to the direct P_{μ} absorption spectra while at the same time a drastic enhancement in sensitivity can be obtained. Defect densities were determined, generally from the more prominent 2nd harmonic spectra, after careful calibration via optimized standard 1st harmonic measurements. In practice, the latter densities were obtained through double numerical integration of observed dP_{μ}/dB spectra (P_{μ} is the applied microwave power), either directly or simulations of these, measured with properly reduced P_{μ} and amplitude of the applied sinusoidal modulation of B to avoid signal distortion. For this purpose, use was made of a comounted calibrated Si:P marker sample, also serving as g reference with $g(4.2\text{ K}) = 1.99869 \pm 0.00002$. The

attained absolute and relative accuracies are estimated at about 20% and 10%, respectively.

3. Experimental results

The main result addressed in this work concerns a so far unreported broad distinct ESR pattern -labeled as H5- observed in part of the (100)Si/hafnia films, the intensity of which shows outspoken sensitivity to applied PD treatment(s). The signal is illustrated in Fig. 1 showing the computed derivative of a typical Q-band 2nd harmonic ESR spectrum detected at 25 K on an ALD HfO₂/(100)Si entity subjected to VUV. Rather than the as-observed spectrum, it is presented this way to better expose spectral g matrix characteristics more in line with ESR convention. The spectrum, showing no field-angle dependence, is recognized as a powder pattern, which, as shown by the dashed curve, could be well simulated by the powder pattern of a spin S=1/2 defect of orthorhombic symmetry using the principal g values $g_1=1.880$, $g_2=1.907$, and $g_3=1.980$ -much reassuringly, the same as obtained within experimental accuracy from K-band observations made on physically the same samples.

As to MOCVD (100)Si/HfO₂ entities, no ESR signal is observed for the as-deposited state. But after positive charge injection treatment, a prominent ESR signal is activated, as well as after VUV or ⁶⁰Co γ irradiation, though with different (lower) ESR signal intensity: an orthorhombic powder pattern signal very similar to the one ascribed above is observed, albeit, as inferred from signal simulation, showing slightly different principal g values and somewhat variation in the width of the Gaussian broadening functions applied for spectrum simulation. Yet, over all ALD and MOCVD grown (100)Si/HfO₂ structures studied for all post-deposition treatments applied, the principal g values are comprised in the specification $g_1 = 1.880 \pm 0.006$, $g_2 = 1.900 \pm 0.007$, $g_3 = 1.981 \pm 0.0015$.

These inferred g matrix values, noticeably below the free electron g value ($g_e=2.00232$), refer to an electron-like state. The powder pattern nature of the signal indicates it to originate from the disordered HfO₂ layer, i.e., no c-Si substrate or interface related defect.

Spectroscopically, it may be added that given the spread outwidth of the powder pattern observed, in combination with the limited number of defects enclosed in an actual ESR sample, the signal appears hard to detect using the conventional 1st harmonic ESR mode.

Interestingly, as to the charge injection influence on ESR intensity, a systematic behavior is observed as a function of corona charging, as illustrated in Fig. 2. This bears out the signal to be substantially enhanced (~3–4 times) by positive corona treatment, while being drastically reduced, sometimes to the detection limit, by the negative polarity. A

maximum defect density of $\sim 4.5 \times 10^{14} \text{ cm}^{-2}$ is inferred, corresponding to the substantial volumetric density in HfO₂ of $\sim 4.5 \times 10^{19} \text{ cm}^{-3}$ if assuming uniformly distributed defects. The observed charge injection relationship is perhaps much relevant when put in the perspective of the results of previous electrical (capacitance-voltage) trapping analysis

[20]: positive charging was observed for HfO₂ films in ALD and MOCVD (100)Si/HfO₂ structures, in contrast with the NCVD ones, Fig. 1. Derivative second harmonic Q-band phase-quadrature H5 spectrum observed at 25 K on ALD-grown p-(100)Si/HfO₂(100 nm) subjected to VUV irradiation. The dashed curve represents a powder pattern simulation using the principal g values $g_1 = 1.880$, $g_2 = 1.907$, and $g_3 = 1.980$, and Gaussian broadening functions of peak-to-peak width $\Delta B_{pp}=45 \text{ G}$, 30 G , and 14 G for the g_1 , g_2 , and g_3 nodes, respectively. charging negatively.

Perhaps pertinently too, we may recall here NCVD to concern a H-free process, unlike ALD and MOCVD which are known to result in HfO₂ films H-rich to the ~1% level.

Regarding the appearance and detectability of the revealed defect, there are various other noteworthy aspects. For one, in the as grown state, the ESR signal, albeit in weak intensity, is only observed in the ALD samples. This situation changes for the MOCVD growth, the signal becoming only observable upon positive corona, VUV or ⁶⁰Co γ treatment. However, no signal could ever be detected in NCVD samples, after whatever PD treatment applied. Also, after 'tuning on' by positive charge injection, the signal is observed to decay (typically in days) to the detection limit for the sample left in room ambient. Additionally, the signal is also found to disappear for annealing at $T \geq 500 \text{ }^\circ\text{C}$ or UV treatment.

Finally, for reasons of comparison, ALD ZrO₂ films (fabricated from ZrCl₄ and H₂O precursors) were studied as well. The elements Hf and Zr show close chemical similarity; The properties of bulk ZrO₂ and HfO₂ are very alike, and at the rise of the high-κ era in Si device technology over a decade ago, both dielectrics have been intensely investigated, almost in tandem, as potential substitute for the conventional SiO_x(N_y) gate insulator since they are thermodynamically stable in contact with Si. However, no ESR signal could be observed from ZrO₂ films after whatever PD treatment.

4. Interpretation

The fundamental quest arises about the atomic nature of the defect; Although ESR emerges as the technique of choice for point defect identification, with no hyperfine structure resolved, identification has to rely principally on provided g matrix values and related defect symmetry. With respect to defects in HfO₂, this has fortunately come within reach thanks to theoretical progress [3,4,13]. In particular, using an embedded cluster method within a density functional theory approach, g matrices have been calculated for 1+charged 3 and 4-fold O vacancies in monoclinic (m) HfO₂. Yet, focusing on these O vacancy predictions, none of the theoretical results fits the experimental data globally. However, on the basis of its largest g₃ (g_{xx}) value, as well as the extent of the orthorhombicity, the results would be in favor of a 4-fold V_{O4}

+ vacancy → a

4-fold O-vacancy in the 1+paramagnetic (electron) state giving rise to a single occupied level near the middle of the HfO₂ band gap.

Obviously, the interpretation of the currently reported H5 spectrum should also be put in the perspective of prior experimental results.

There have been previous ESR observations on defects in HfO₂, in the form of bulk material and as deposited films, including a wide set of m-HfO₂ powders subjected to ¹³⁷Cs γ-irradiation and grinding [19] and ALD grown (100)Si/HfO₂ (~43 nm) entities (using the Hf(NO₃)₄ precursor) subjected to corona electron charging and unbiased γ-irradiation [22]. Various powder patterns have been observed, including one identified as the interstitial O₂

– ion [22] and others ascribed to CO₂

– radicals

[19] and the Hf³⁺ ion [19,22], similar to the Zr³⁺ ion center in ZrO₂

[23]. However, none these spectra seems to match that of H5: On grounds of the g matrix, the peroxy radical O₂

– type defect is excluded,

as well as the defect ascribed to Hf³⁺ ions. Neither seems the revealed defect like any observed in different m-HfO₂ powders subjected to grinding, ¹³⁷Cs γ-irradiation, and vacuum annealing [19].

In tracing the defect's nature, one more crucial element may be the large volumetric defect densities detected by ESR. Positively charged defects occurring in such densities may be hard to envision (Coulombic interaction) if not present charge compensators (valence-alternation pairs [24]), so the electrically and ESR-detected defect (charge) densities may differ.

5. Conclusions

In summary, with the aim to assess the atomic nature of charge trapping, low-T (4.2–30 K) ESR measurements, using conventional K- and Q-band spectrometry, have been performed on functional HfO₂ films deposited on p-(100)Si by three types of CVD methods using different precursors. In HfO₂ layers grown by ALCVD and MOCVD subjected to ex situ positive charging treatment, this reveals the presence of a defect of orthorhombic symmetry, reaching volumetric densities of up to $\sim 4.5 \times 10^{19} \text{ cm}^{-3}$; Its appearance and intensity shows reproducible and firm correlation with charge injection, i.e., distinct signal intensity increase/decrease with alternate positive/negative charge injection, respectively.

The defect is not observed in HfO₂ films grown by NCVD, nominally an H- and C-free process. The signal is found to be also positively affected by post-growth VUV and ⁶⁰Co γ-irradiation.

The distinctly spread out nature of the H5 ESR signal, linked with the substantial g matrix asymmetry, impedes easy ESR detection despite the large defect densities encountered. No additional correlated hyperfine structure could be resolved in the ESR spectrum, making that the assessment of its atomic origin has to rely mainly on the inferred g matrix data

and charging behavior. Stepping from the available spectroscopic traits, interpretation in the light of previous advanced calculations based on density functional theory of O-vacancy centers in m-HfO₂ suggests that as to the revealed orthorhombic defect, one might be dealing with an oxygen vacancy type center. In that interpretation, though not perfect, its ESR characteristics may be compatible with those anticipated for the 4-fold V_{O4}

+ vacancy on HfO₂. Such defect causes a single occupied level deep in the band gap, and is to be evaluated within the context of previously electrically observed positive charge trapping in Si/hafnia structures grown by atomic layer and metal-organic CVD.

The current study may be viewed as a prospecting attempt, based on spectroscopy with true atomic sensitivity, to assess the basic nature of charge trapping centers in device-grade Si/HfO₂ entities. The results may help shining some light about our insight on the occurrence of the oxygen vacancy in high dielectric constant insulators, which center has been widely advanced as the critical defect in hafnia, but still awaiting conclusive identification. In lack of any resolved ESR hf structure, it is realized this identification will have to rely much on first-principles theory, the route followed in this work.

Acknowledgments

The authors are grateful to S. DeGendt and M. M. Heyns (Imec, Belgium) and S. A. Campbell (University of Minnesota, USA) for support in sample preparation. Part of the work was financially supported by the KU Leuven Research Fund (Project OT/05/31) and the Research Foundation -Flanders (FWO) (grant G.0.0525.05).

Fig. 2. Evolution of the areal density of the ESR spectrum, H₅, as a function of various postdeposition corona charging treatments. The dashed lines interconnect data points to accentuate trends.

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