# Characterization of ZrO2 thin films deposited by MOCVD for high-density 3D capacitors. Broad experience on MOCVD techniques and high-k materials

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Toulouse, 17th October 2008

Dear Editor,

I am pleased to send you the first results of our work on the deposition of ZrO2 by MOCVD on 3D structures. This work was presented at IUMRS-ICEM conference in Sydney this summer 2008 (28th of July – 1st of August 2008). No proceedings were published out of the Symposium P: “Production, Processing and Characterisation of High k Dielectrics”.  I thus decided to submit it to Microelectronics Engineering as I think the subject is relevant to your journal.

Please accept my best regards,

Yours sincerely,

Magali Brunet

# Characterization of $ZrO_2$ thin films deposited by MOCVD for high-density 3D capacitors.

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**Abstract**

The present work deals with high-density integrated capacitors for output filters in future micro DC-DC converters. To reach high capacitance density, 3D structures were created in silicon with DRIE followed by MOCVD of $ZrO_2$ (100 nm thick). The step coverage revealed two deposition regimes: a surface reaction controlled regime for cavities aspect ratio lower than 2 and a diffusion controlled regime for higher aspect ratios. The $ZrO_2$ films present mostly a cubic/tetragonal structure. The permittivity extracted from the measurement is 26.4. These results are discussed with static dielectric responses calculated in literature.

*Keywords:* MOCVD, $ZrO_2$, High-k, thin film, step coverage, 3D structures, MIS capacitor.

## 1. Introduction.

DC-DC converters are necessary for each functionality of low power portable equipments. As the systems have to be as miniaturized as possible, the integration of passive components constituting the output filters (inductors, capacitors, resistors) together with the active chip is of great interest. When talking about integrated capacitors, the current solutions on silicon (MOS or MIM) are not able to produce the capacitance values required for 1W DC-DC converter: more than 1 µF/mm². To increase the capacitance density of integrated capacitors, the first approach is to work on the geometry, in other words reduced dielectric thickness and maximised electrodes area. The second approach concerns the use of a high-k dielectric. The purpose of the presented work is to combine these two approaches.

3D capacitors structures were realised with deep cavities network etched by DRIE (Deep Reactive Etching) in a high conductivity silicon substrate (20 mΩ.cm). The $SiO_2/Si_3N_4$ standard dielectric stack [1] was replaced by $ZrO_2$ with a reported permittivity ($\varepsilon_r$) for thin films between 17 and 30 [2-4]. This dielectric material presents also a good breakdown voltage (3-10 MV/cm) [4,5] which is of great importance when designing capacitors for DC-DC converters applications: the component should sustain at least 15 V. The dielectric static response of $ZrO_2$ was calculated by Zhao et al. [6]. It is much higher ($\varepsilon_{r(c)} = 37$ and $\varepsilon_{r(t)} = 38$) for the cubic and tetragonal phase respectively than for the monoclinic phase ($\varepsilon_{r(m)} = 20$). Tetragonal/cubic phases have therefore to be present if high capacitance densities are to be reached.

$ZrO_2$ was deposited by MOCVD (Metal Organic Chemical Vapour Deposition) in order to allow step coverage. The films were first characterized structurally: phase, stoichiometry, contamination, step coverage. In a second part, MIS structures were fabricated and the electrical properties of the planar films are discussed.

## 2. Experimental.

High conductivity silicon substrates ($N_d = 10e^{18}$ at/cm$^3$) were used as the bottom electrodes of the capacitors. Deep cavities (40 µm maximum) with high aspect ratio up to 10, arranged in a dense and regular network were first etched with DRIE to increase the bottom electrode surface.

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The $ZrO_2$ films were then deposited by liquid injection MOCVD from $Zr_2(O^iPr)_6(thd)_2$ precursor evaporated at 240°C. The following deposition parameters were used: oxygen flow (0.05 l/min), substrate temperature (525°C), injection frequency (1 Hz), pressure (less than 100 Pa). Thus, uniform films (without any cracks) were obtained. The $ZrO_2$ films deposited on silicon (100) were characterized structurally by X-ray diffraction (XRD) in w-2Θ configuration. The $ZrO_2$ thickness was measured by ellipsometry and by SEM on the cross-section of the cavities.

## 3. Results and discussion.

Figure 1 shows the XRD patterns of the as-deposited $ZrO_2$ film (550°C) and after an annealing step at 900°C under $O_2$. Peaks were indexed according to JCPDS files (tetragonal n°17-0923, cubic n°49-1642 and monoclinic n°37-1484). After deposition, the polycrystalline films revealed either a tetragonal or cubic structure, signed by two peaks at $2\theta$ = 30° and 35°. After annealing, a peak at 31.3° was present which is the signature of the monoclinic phase.

In parallel, the 3D coverage was observed in cavities with different depths (from 10 to 40 µm) and widths (from 2 to 8 µm). Figure 2 shows the SEM picture of a typical thickness measured on the cross-section of silicon cavities.

To get a better understanding of the deposition regimes in the cavities, the thickness evolution was plotted versus the cavity aspect ratio (depth/width). Figure 3 shows the thickness normalised to the top thickness ($e/e_0$) versus the cavity aspect ratio. It is shown that the $ZrO_2$ thickness decreases to 30% of its surface value when the aspect ratio of the cavity reaches 2. For aspect ratio higher than 2, the thickness decreases only slightly. This may be interpreted by two different chemical reactions or by the existence of two regimes: a surface reaction limited regime for low aspect ratios (<2) and a diffusion limited regime for aspect ratio higher than 2. To favour the later regime, the mean length path of molecules should be increased. In theory, this can be achieved by decreasing the pressure.

Electrical characterization of the as-deposited $ZrO_2$ films were done on planar MIS structures: low resistivity silicon substrate (20 mΩ.cm) as the bottom electrode and gold as the top electrode. The metallic contact for the bottom electrode was a SbAu layer on the backside of the wafer. The C(V) characteristics at 1 MHz shown on figure 4 are representative of a MIS structure with n-type silicon with inversion at negative bias and accumulation at positive bias. Four capacitors on the same sample were measured. The shifts in the C(V) curves reveal the presence of interface states and traps in the oxide. The accumulation capacitance is 2.2 nF/mm². Although C(V) characteristics are helpful for separating the contributions of the semiconductor substrate and the oxide in a MIS structure, in terms of the component characteristics however, the silicon substrate has to be doped further to avoid capacitance variation due to depletion. Furthermore, doping will reduce the series resistance and therefore will help to reduce power losses by Joule effect in the component.

I(V) curves measured with a Keithley 4200 SCS, revealed that the $ZrO_2$ films could not sustain the 15V required. Figure 5 shows the current density versus bias for a MIS capacitor. The high current densities measured are mainly due to extrinsic defects.

Frequency sweeps were then done with a HP-4294A impedance analyser on the capacitors: the module and phase of the impedance with 200 mV of signal oscillations are shown on figure 6a and 6b. In the frequency range of interest (500 kHz – 10 MHz), for this small-signal characteristics, the leakage current in the dielectric layer has no effect on the capacitor behaviour.

An analytical model (figure 7) was developed to fit the measurements and to eventually extract the permittivity of the sole $ZrO_2$ material. In this model, are represented: the capacitance $C_{ox}$ given by the $ZrO_2$ layer, the capacitance $C_{inv}$ (41 pF) due to the depletion of the n-type silicon, the leakage resistance ($R_p$ = 2.1 MΩ) and the capacitance-resistance couple ($R_1$ – $C_p$) due to charges in the oxide. From $C_{ox}$, the permittivity of the $ZrO_2$ layer was extracted: it is equal to 26.4. The measured permittivity of the as-deposited $ZrO_2$ film doesn't reach the theory values ($\varepsilon_{r(c)}$ = 37 or $\varepsilon_{r(t)}$ = 38 [6]). It can be explained by several factors: first, the presence of a native oxide ($\varepsilon_r$ = 3.9) at the interface with the silicon substrate, with an estimated thickness of 1.5 nm. Then silicates might also be present at the interface that would reduce even more the overall permittivity. Further investigation will be done with TEM-

EELS (Transmission Electron Microscopy - Electron Energy Loss Spectroscopy) to observe the $ZrO_2$/Si interface. Another explanation of the lower permittivity could be found in the texture of the film. In particular, if the film grows with a preferred z-axis orientation perpendicular to the surface, the permittivity of the tetragonal phase would be degraded (15 according to Zhao et al [6]). Pole figures measurement on the film could help understanding this particular point.

In conclusion, the measured permittivity can still be attributed to the tetragonal/cubic phase as the value is much higher than the expected value for the monoclinic phase (20).

## 4. Conclusions.

$ZrO_2$ was deposited by MOCVD in high aspect ratio silicon cavities in order to fabricate high-density 3D capacitors.

Tetragonal/cubic phase was present in the films with the chosen conditions of MOCVD. Step coverage of $ZrO_2$ in the cavities was not fully obtained: two regimes of deposition were observed. In the future, diffusion-controlled regime should be made predominant in order to reach perfect conformal deposition in high aspect ratio cavities. Planar MIS capacitors were tested electrically. The relatively good permittivity (26.4) of $ZrO_2$ was attributed to the tetragonal/cubic phase. Further structural and chemical investigations in the structure of the films are required in order to determine why the permittivity is lower than the calculated value.

The use of $ZrO_2$ combined with 3D deposition in high aspect ratio cavities will lead to the realisation of very high-density capacitors. Future work will focus on the characterization of the 3D capacitors with $ZrO_2$ as dielectric.


## Acknowledgements.

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Fig. 1. XRD 2theta pattern for $ZrO_2$ film as deposited and annealed at 950°C under $O_2$.
Fig. 2. Cross-sectional SEM pictures of silicon 43 µm deep, 10 µm large cavities with close-up views of $ZrO_2$ layer at the top (110 nm) and at the bottom of the cavities (35 nm).
Fig. 3. Normalized thickness $e/e_0$ versus cavity aspect ratio.
Fig. 4. C(V) characteristics at 1MHz of four 100 µm x 100 µm MIS capacitors (same sample).
Fig. 5. Current density versus bias for a 100 µm x 100 µm MIS capacitor.
Fig. 6. Impedance measurement a) module and b) phase of the MIS capacitor.
Fig. 7. Analytical model of MIS capacitor.

Figure 1
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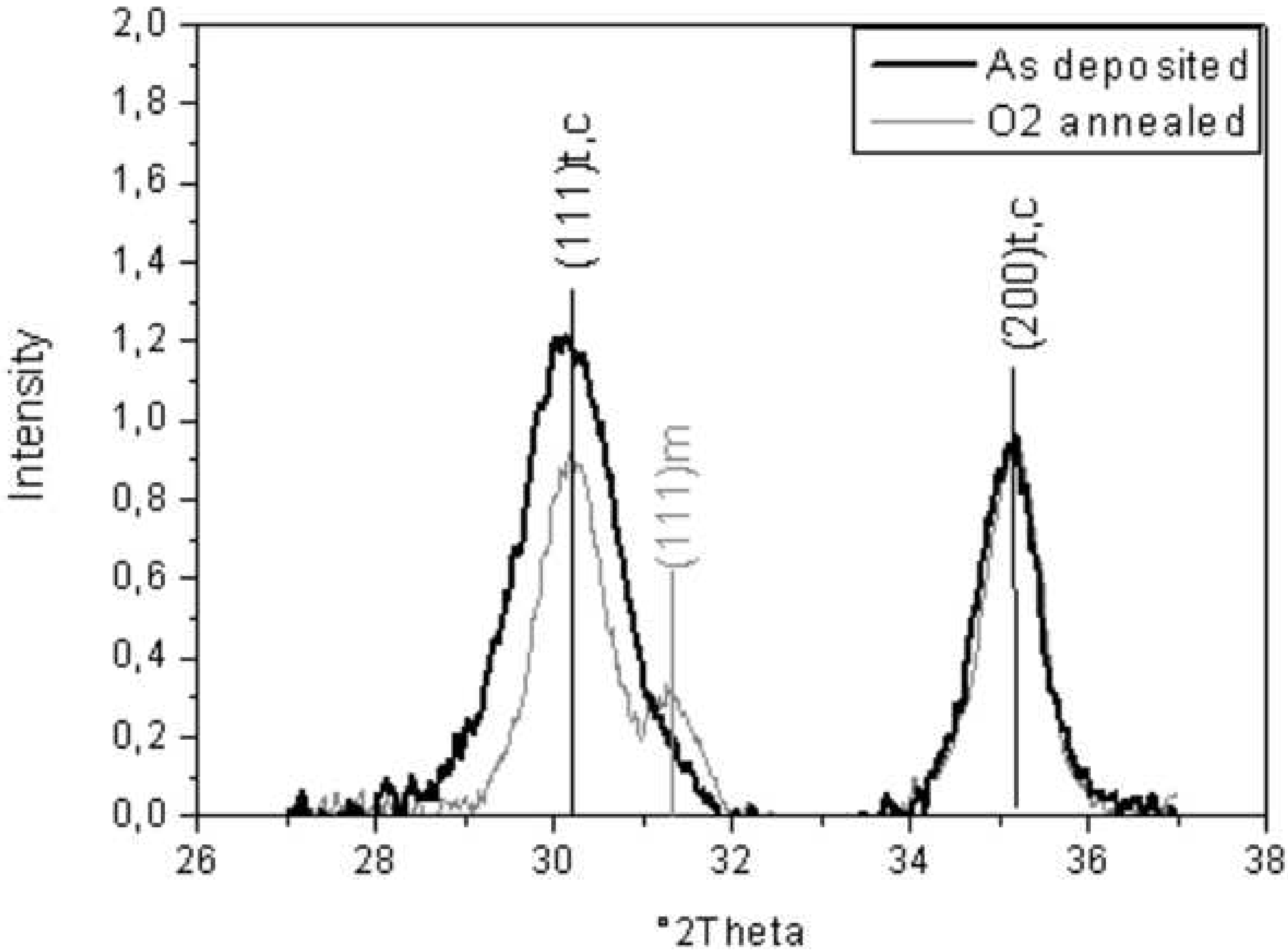

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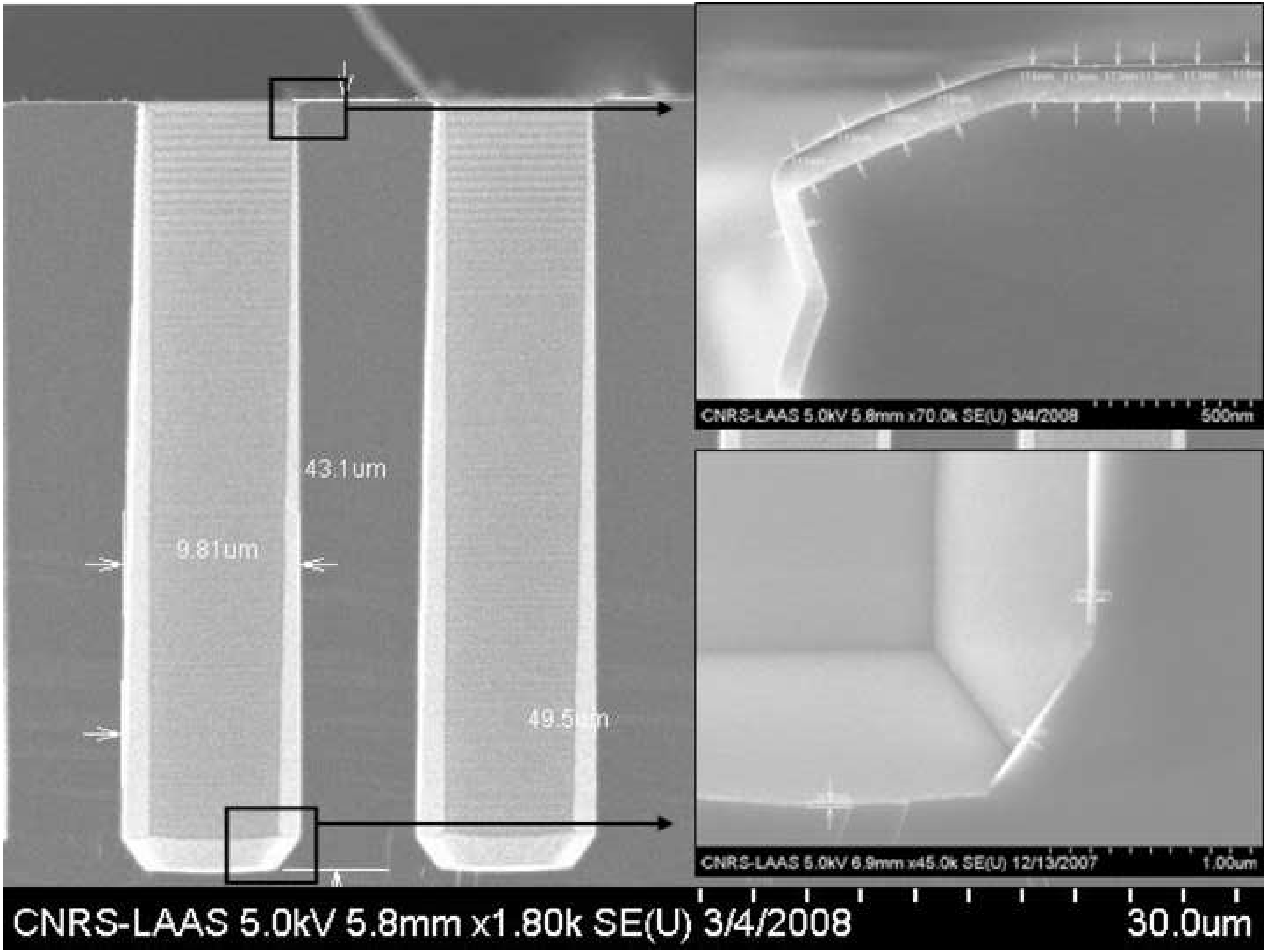

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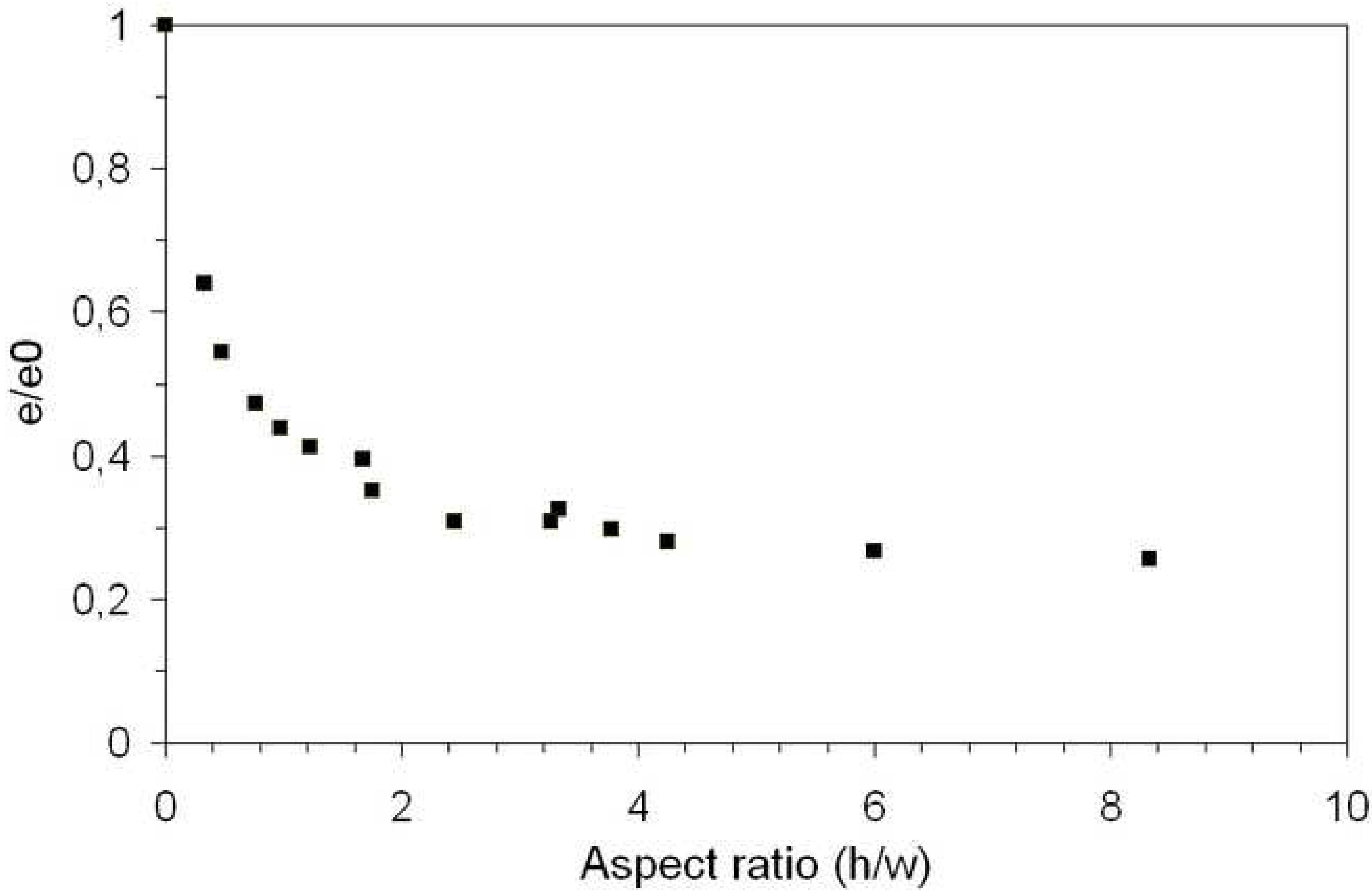

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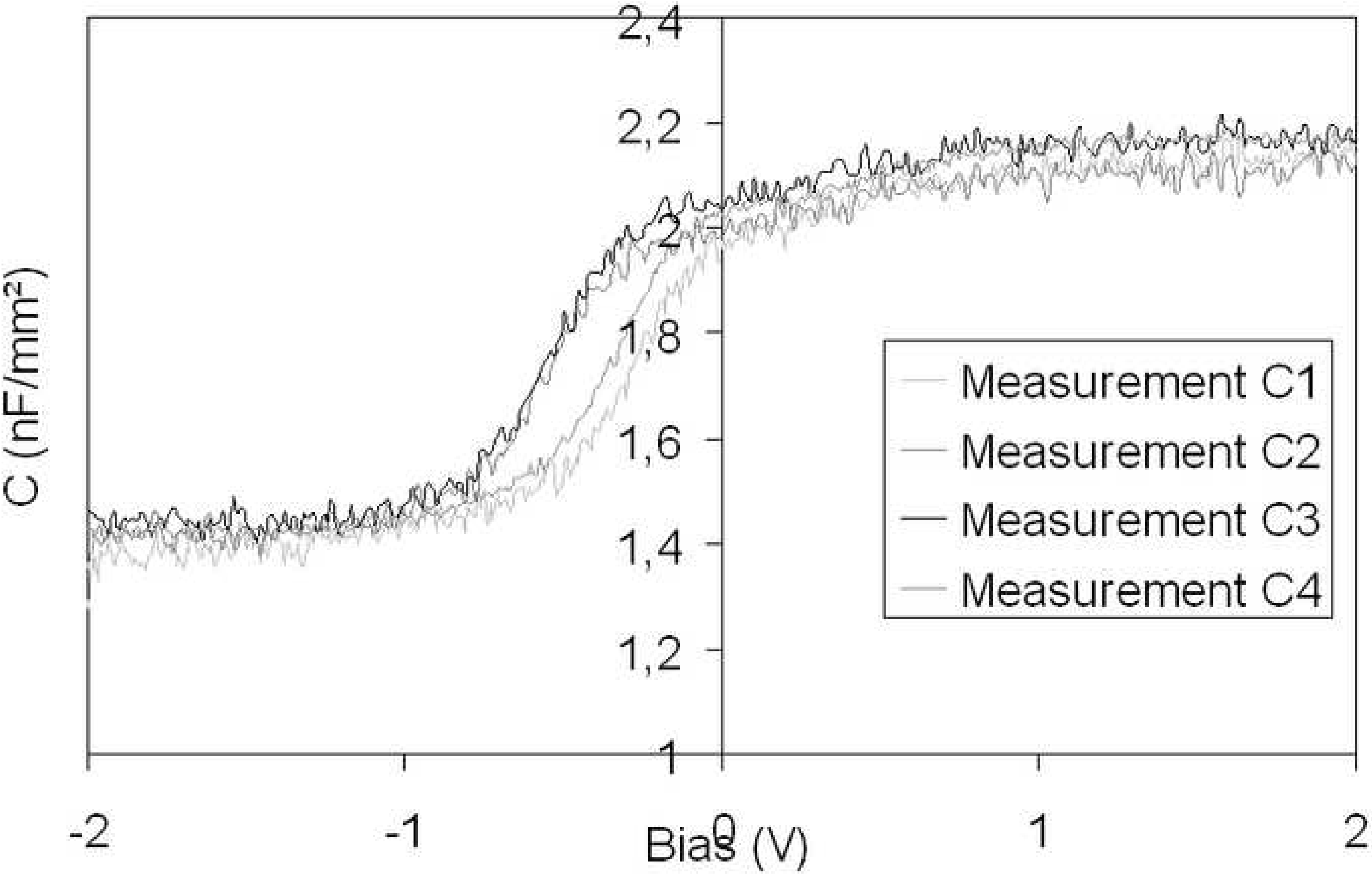

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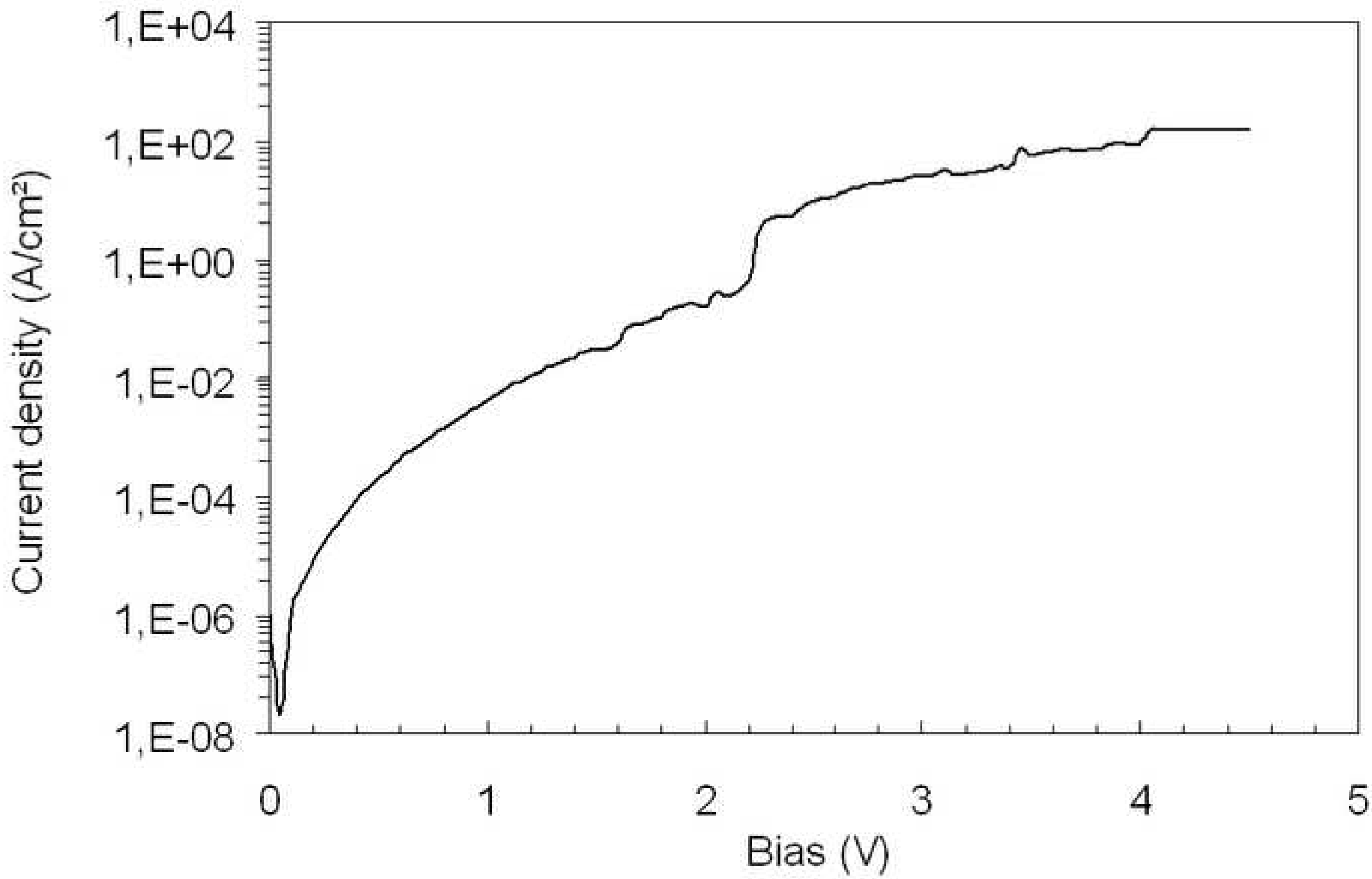

Figure 6a
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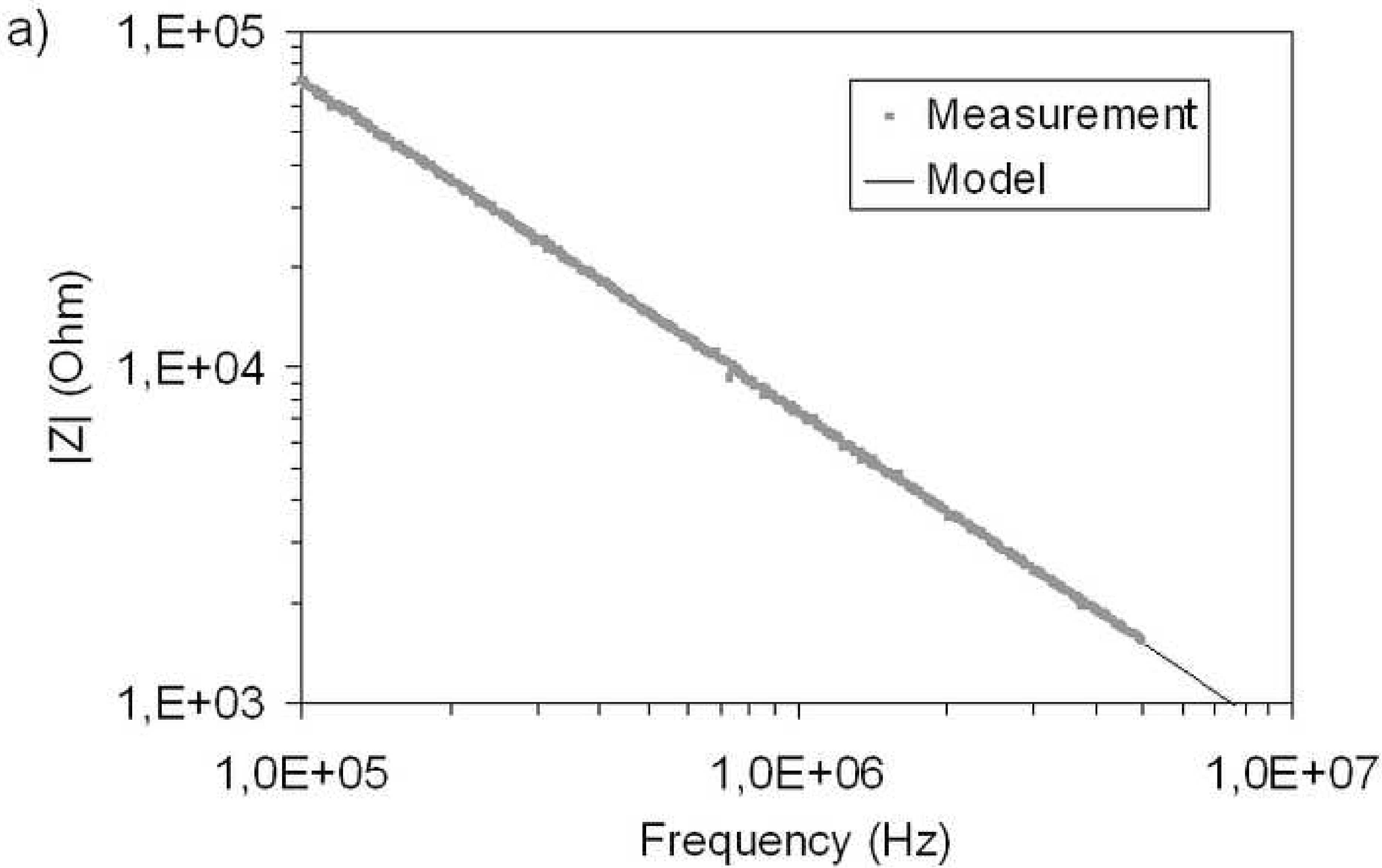

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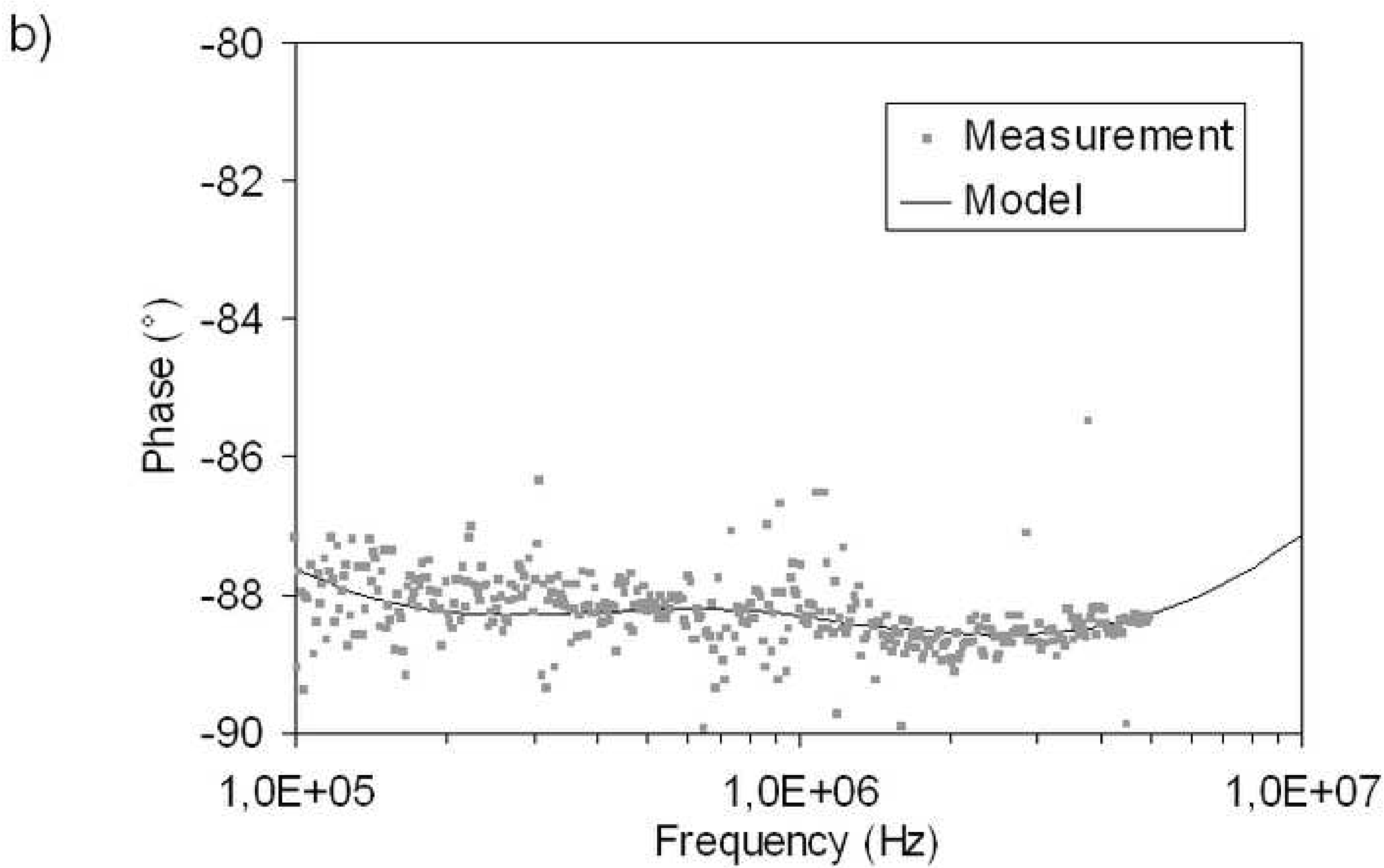

Figure 7

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