Investigation of Embedded Perovskite Nanoparticles for Enhanced Capacitor Permittivities

Andreas Krause,* Walter M. Weber,† Darius Pohl,‡ Bernd Rellinghaus,‡ Marcel Verheijen,§ and Thomas Mikolajick†∥

†NaMLab gGmbH, Noethnitzer Strasse 64, 01187 Dresden, Germany
‡Institute for Metallic Materials, Leibniz Institute for Solid State and Materials Research (IFW) Dresden, P.O. Box 270116, 01171 Dresden, Germany
§Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
∥Institute of Semiconductors and Microsystems, Dresden University of Technology, 01062 Dresden, Germany

Supporting Information

ABSTRACT: Growth experiments show significant differences in the crystallization of ultrathin CaTiO₃ layers on polycrystalline Pt surfaces. While the deposition of ultrathin layers below crystallization temperature inhibits the full layer crystallization, local epitaxial growth of CaTiO₃ crystals on top of specific oriented Pt crystals occurs. The result is a formation of crystals embedded in an amorphous matrix. An epitaxial alignment of the cubic CaTiO₃ ⟨111⟩ direction on top of the underlying Pt {111} surface has been observed. A reduced forming energy is attributed to an interplay of surface energies at the {111} interface of both materials and CaTiO₃ nanocrystallites facets. The preferential texturing of CaTiO₃ layers on top of Pt has been used in the preparation of ultrathin metal–insulator–metal capacitors with 5–30 nm oxide thickness. The effective CaTiO₃ permittivity in the capacitor stack increases to 55 compared to capacitors with amorphous layers and a permittivity of 28. The isolated CaTiO₃ crystals exhibit a passivation of the CaTiO₃ grain surfaces by the surrounding amorphous matrix, which keeps the capacitor leakage current at ideally low values comparable for those of amorphous thin film capacitors.

KEYWORDS: perovskites, nanocrystallites, dielectrics, local epitaxy, surface energy

1. INTRODUCTION

Perovskites are a well-known group of materials with multifunctional properties such as high permittivity,1–4 ferro- and piezoelectricity,5,6 superconductivity,7,8 and ferromagnetism.9 With small substitutions of the perovskite crystal structure, the conductivity can be tuned from insulating toward metallic behavior, for example, for colossal magnetoresistance11 or transparent conductors.12 All these perovskite materials and their properties have opened access to considerable research activities and multiple applications.

Previous calculations for perovskites done in literature investigate the surface energy of specific surfaces or ferroelectricity at interfaces or grain boundaries by introducing lattice strain. Recent experiments on perovskites accessed the nanoscale region with the growth of nanowires13,14 and nanoparticles.15,16 So far, CaTiO₃ has not found its way in the preparation of nanostructured devices. Recent results of strain engineering on typically paraelectric CaTiO₃ show ferroelectric behavior at the grain boundaries17,18 or ferroelectricity at surfaces.19 The possibility to control the number and surrounding of grain boundaries can therefore be used for future device applications.

In this work, we show a detailed study of perovskite nanocrystallites surrounded by an amorphous matrix for the case of sputter deposited CaTiO₃. Capacitors with those embedded nanocrystallites exhibit an intermediate permittivity of 50 and above between the permittivity of approximately 10⁵ in a fully crystalline layer and 28 for amorphous CaTiO₃ layers.20 Pt is a suitable material for epitaxial growth of perovskites21,22 with a lattice constant comparable to CaTiO₃.23 Besides the good lattice match, the selective growth of the nanocrystallites takes advantage of the different surface energies of CaTiO₃ and Pt facets. Consequential differences in crystal formation energy result in a preferential growth of crystalline CaTiO₃ nanocrystallites in ⟨111⟩ direction on top of the underlying Pt ⟨111⟩ surface texture. The embedded nanocrystallites further exhibit a surface passivation by the surrounding matrix of amorphous CaTiO₃. We show that this effect has been used to significantly reduce leakage currents in 10–30 nm thick metal–insulator–metal (MIM) capacitor stacks. This is an important step to solve the typical trade-off
between crystallinity and high permittivity on the one hand and to low leakage current that requires amorphous films on the other hand for dynamic random access memory (DRAM) capacitors.24,25 This trade-off is nowadays eluded with the use of multilayers,26 with the disadvantage of low permittivity layers in serial capacitor arrangement.

2. EXPERIMENTAL METHODS

The CaTiO3 layers were sputtered on top of 4 × 4 cm substrates in a 6 in. adapter plate. These substrates consist of an electrically conducting electrode of sputter deposited Pt on top of TiN at 100 °C (p = 1.1 × 10−3 mbar, 25 sccm Ar for Pt; p = 1.2 × 10−3 mbar, 20 sccm Ar, 4.5 sccm N2 for TiN) on a highly As-doped (1 × 1019 cm−3) Si substrate. For oxide deposition, the substrates are located axis-on-axis approximately 24 cm from the 3 in. target surface to achieve high thickness uniformity. To enable the formation CaTiO3 nanocrystallites in an amorphous matrix, the deposition of the CaTiO3 layers with different thicknesses has been done at varying temperatures between 550 and 600 °C substrate temperature. This is slightly below the temperature of approximately 650 °C for which full crystallization of the whole layer on top of a Si substrate was achieved in previous investigations.27 The deposition rate of CaTiO3 was approximately 0.17 nm/min.

To allow the electrical characterization of the samples, a complete MIM capacitor stack was created with the deposition and structuring of a top electrode (15 nm layer thickness) consisting of TiN or Ru (p =1.2 × 10−3 mbar, 20 sccm Ar for Ru) to account for different work functions. The top electrode is structured with the help a metal hard mask as well as removal of TiN with wet etching (5 min in 10:20:50 mL of NH3 (25%):H2O2 (30%):H2O at 50 °C) and reactive ion etching with O3 plasma of Ru under the formation of volatile RuO2. The top electrode structure consists of 70 circles with different diameter (110 μm–450 μm) per die with 6 dies per sample.

To verify the formation of crystallites in the layer, capacitance voltage measurements on 35 of these MIM capacitors were performed to extract the effective permittivity εr. This was done at 100 kHz with 50 mV small signal in a shielded semi-automated probe station. Only capacitors with a dissipation factor below 0.1 have been used for extraction of the capacitance to ensure the validity of the used parallel capacitance measurement model (Cp-D). The measured permittivity is the result of a mixture of permittivities of amorphous and crystalline CaTiO3. The same setup has been used to measure the leakage current of the other 35 capacitors and allowed a correlation between both functions. The leakage current measurement was performed with a 5 s delay between each measurement step to virtually eliminate relaxation currents. The positive voltage was applied to the conducting substrate via the probe station chuck. The maximum voltage applied has been set to a voltage of approximately 20% below the breakdown voltage.

Selected samples have been further prepared for high-resolution transmission electron microscopy (TEM) measurements.

3. EXPERIMENTAL RESULTS

The crystallization and therefore the permittivity can be controlled by the thermal budget during deposition as well as the oxide layer thickness. The transition from partially crystalline to fully crystalline layers is governed by a sensitive interplay between both the thermal budget and layer thickness. As shown later in Figure 5, the deposition time plays no significant role in the degree of crystallization. CaTiO3 layers thicker than a critical thickness for a chosen deposition temperature crystallize completely. At lower thicknesses, the crystallization is inhibited. This is comparable to experiments using capacitors with ultrathin ZrO2 layers on top of polycrystalline TiN and single crystalline Si substrates.28,29 The effect has been related to an inhibited homogeneous crystallization due to the reduced formation energy according to the work of Zacharias et al.30 and Wei et al.31 Nevertheless, the system with a polycrystalline bottom layer with a comparable lattice to the CaTiO3 layer has so far known not been investigated in experiments before.

Figure 1 shows a bright field transmission electron microscopy (BFTEM) cross-sectional image of a CaTiO3 layer deposited at 600 °C on top of polycrystalline Pt. The darker parts indicate CaTiO3 crystallites embedded in an amorphous matrix of CaTiO3 as brighter areas. The CaTiO3 nanocrystallites exhibit an inverse pyramidal shape starting at the Pt bottom electrode. Figure 1 also shows that a significant PtSi formation has been prevented by the deposition of a thin 3 nm TiN layer as a conducting diffusion barrier in between Pt and the Si substrate.

In Figure 2, a detailed high-resolution TEM (HRTEM) micrograph shows the interface between a single isolated CaTiO3 crystallite and the underlying Pt surface. There is a correlation between the surface orientations of both materials (similar results for another isolated crystallite are shown in Figure S2, Supporting Information). From a specific region of the interface (red rectangle), a fast Fourier transform (FFT) has been taken to allow to extract the crystal orientations and the correlation of both lattices. The FFT pattern displays a [110] zone axis pattern of the Pt crystal with a (111) axis parallel to the Pt surface normal, as expected from a (111) texture of the Pt film. The other strong spots correspond to the CaTiO3 lattice planes visible in the CaTiO3 crystal and can be assigned to (220) and (440), respectively. The accuracy of the FFT pattern with both Pt and CaTiO3 reciprocal lattice points does not give enough information for the unique assignment of the CaTiO3 zone axis. Nevertheless, with an increased contrast, it was possible to extract the relevant orientations of cubic CaTiO3 (Figure S3, Supporting Information). As a result, both Pt and CaTiO3 crystals are seen in Figure 2 from the [110]
zone axis. The different intensities of the CaTiO₃ reflexes originate from the deformed cubic structure of CaTiO₃ crystal where crystal symmetries are broken. The CaTiO₃ spots coincide within 90° to the position of the {220} spots of the Pt crystal. Other orientation relations between CaTiO₃ crystallites and the Pt layer have not been observed. The low lattice mismatch between Pt (a = 0.392 nm) and CaTiO₃ (a = 0.384 nm) suggests a selective-area epitaxial growth of CaTiO₃ on top of Pt with 2.0% lattice mismatch.

Figure 3 schematically depicts the lattice in cross-sectional and top views of the CaTiO₃/Pt interface, as it correlates to the TEM image of Figure 2. Both the Pt face-centered cubic (fcc) lattice and the CaTiO₃ crystal are displayed along the (110) zone axis. The Pt surface is terminated by the {111} lattice planes. The FFT of CaTiO₃ shows the (111) lattice planes of the cubic CaTiO₃ lattice. The transformation between the orthorhombic and cubic unit cells of CaTiO₃ is a simple vehicle to calculate the correct correlation between both lattices (Table S1, Supporting Information). As discussed above, the correct zone axis toward the visible CaTiO₃ planes is not clearly extractable from Figure 2 due to the limited reciprocal lattice points. Taking the cubic CaTiO₃ unit cell, the view along the (110) zone axis allows an observation of the (111) lattice plane. In this case, the CaTiO₃ surface is either terminated by the CaO₃ plane or the Ti plane toward the Pt (111) surface. The oxide termination and the formation of the Pt–O bonding have been calculated previously for the comparable SrTiO₃ lattice. That supports the CaO₃ termination of the CaTiO₃ interface, which has been assumed in Figure 3. Finally, due to the comparably good lattice match of both materials, the depicted simplest correlation of (111) CaTiO₃ and (111) Pt is expected and shown in Figure 3b.

The correlation between CaTiO₃ and Pt along the (111) direction is a hint toward an epitaxial growth of CaTiO₃ crystallites. Interestingly, no orientation relation has been observed other than the one identified in Figure 2 and in Figure S2 (Supporting Information).

4. MECHANISM FOR PARTIAL NUCLEATION

The partial crystallization of CaTiO₃ cannot be solely explained by the good epitaxial relationship between Pt and CaTiO₃. Due to the comparable (cubic) crystal structure of Pt and CaTiO₃, the lattice mismatch of similar directions is identical, and the lattice plane distances d₁₁₁ are equal in this case. For all crystal lattice directions, the same epitaxial relationship exists, and CaTiO₃ should crystallize completely even on a polycrystalline Pt surface. X-ray diffraction (XRD) measurements indicate, besides the {311} reflex, a {111} texture along the surface normal of the prepared Pt layers (Figure S4, Supporting Information). This could cause the growth of an increased number of CaTiO₃ crystallites, as shown in Figure 1, but does not explain why the whole CaTiO₃ layer does not crystallize completely. The texture of the Pt grains does not imply the state of each Pt surface facet; the roughness indicates a deviation from the {111} Pt surface facet to other indices. These different surface facets may inhibit the continuous CaTiO₃ crystallite growth. The observed partially crystalline CaTiO₃ layer suggests that the forming energy of CaTiO₃ crystals is different for various Pt facets, with a preferred nucleation on top of the Pt {111} facet. Due to the very low deposition rate of 0.17 nm/min at elevated temperatures, the deposited CaTiO₃ is expected to behave in a thermodynamically controlled manner, and the role of kinetic processes to crystallization is negligible. This is supported by the observation that the preferred crystallization is maintained for thicker films that experience a significantly higher thermal budget, as determined by the constant deposition temperature and deposition rate.

According to literature, the nucleation and texture of crystallites are mainly influenced by the underlying substrate and the interface properties. The orientation and growth mode are determined by the involved interface and surface energies. These depend primarily on the strength and nature of the chemical bonds between film and substrate atoms on the one hand and the film atoms on the other hand. The observed preferential growth of (111) CaTiO₃ crystallites on top of (111) Pt is most likely influenced by the differences in surface energies. Although we do not know the exact contribution of the surface energy to the crystallite formation of CaTiO₃, we see the differences as a first approach for explaining the partial growth.

Pt tends to form {111} facets at higher temperature due to the lowest surface energy of the {111} facet. The calculated surface properties of CaTiO₃ facets are briefly summarized in Table S2 (Supporting Information). For all A²⁺B⁴⁺O₆⁻ perovskites (CaTiO₃, SrTiO₃, PbTiO₃, SrZrO₃, BaZrO₃, etc.), the (001) surface exhibits the lowest surface energy.

In growth experiments with SrTiO₃ instead of CaTiO₃, epitaxial growth of SrTiO₃ had been done on top of Pt or vice versa. Nevertheless, differences in growth energy contribution on various surfaces had not been observed for this system. As reported from Asthagiri et al. for the SrTiO₃/Pt system, the polar {111} and {110} surfaces form significantly stronger interfaces than the {100} nonpolar surface. Therefore, and according to the simulated surface energies in Table S2 (Supporting Information) for the cubic CaTiO₃ surfaces, the {111}-terminated CaTiO₃ surface with its largest surface energy is supposed to be the reason for the unique epitaxial formation of a crystalline interfacial CaTiO₃ layer. The forming energy of the first CaTiO₃ crystalline monolayer is reduced and results in a seed layer for the epitaxial growth of CaTiO₃ at deposition temperatures below the bulk crystallization temperature. The reason for this restricted local reduction is not clear, but we suppose that the surface energy of CaTiO₃ with the formation of the strong bindings between CaTiO₃ and Pt along the {111} interface allows a preferred crystallization. Other
areas without a "crystalline" monolayer of CaTiO₃ stay amorphous in the further layer growth. While a \{110\} surface of CaTiO₃ exhibits just a bit lower surface energy, the reduction of the \{110\} Pt surface facets at elevated temperatures may prevent any observation of an epitaxial growth of \{110\} CaTiO₃.

For the further crystallite growth, it cannot be concluded that a closed crystalline layer grows in the (111) direction. However, given the nanometer size dimension of the nucleation areas, the line energies at the circumference of the nucleated layer have a strong contribution to the formation energy of the layer. This is a size effect that roughly considers the number of bonds at the interfacial surface. To this end, we propose that small CaTiO₃ crystallites nucleate with \{110\} facets; although, our TEM analysis does not provide the exact facet orientation. The inverse pyramidal structure can be attributed to the \{100\} passivated surfaces to lower the formation energy of the CaTiO₃ crystal. This is similar to the nucleation of Si nanowires described by Schmidt et al.⁴⁹ The crystallite—amorphous interface exhibits a low surface energy formation with \{100\} CaO or TiO₂ termination. This results in the inverse pyramidal-shaped nanocrystallites, as shown in Figure 1. This is a deviation to the heterogeneous nucleation with the formation of free-standing pyramidal and dome-like crystals observed for PZT and other materials due to island growth.⁵⁰–⁵² The conclusion is that the \{111\} surface of CaTiO₃ with its largest surface energy is preferred for the epitaxial growth along the \{111\} CaTiO₃/Pt interface. As all grown embedded crystallites exhibit the same orientation, the full layer will show epitaxial-like behavior.

When going to higher deposition temperatures or thicker samples with a full crystallized CaTiO₃ layer and homogeneous nucleation, the preferential growth on the \{111\} surface cannot be distinguished in the entire crystallized CaTiO₃ layer.

5. EMBEDDED NANOCRYSTALLITES IN AN ULTRATHIN CAPACITOR STACK

5.1. Electrical Characterization. The embedded nanocrystallites of CaTiO₃ have been prepared in a thickness series of CaTiO₃ in a MIM capacitor stack. CaTiO₃ was deposited at a temperature of 550 °C on top of the polycrystalline Pt electrode. The Ru top electrode was deposited afterward at 100 °C and structured with the help of reactive ion etching. Except for the different deposition time of CaTiO₃, all other deposition conditions have been kept constant. Figure 4 shows a single isolated crystallite in a complete ultrathin MIM capacitor arrangement, deposited at 550 °C. The comparatively elevated deposition temperatures result in the formation of crystallites, even for the thinnest layers. The preferential epitaxial growth is not limited by the oxide thickness.

Figure 5 shows the permittivity evolution for the different thicknesses. The permittivity values have been extracted from a linear fit of the inverse capacitance over thickness by neglecting any interfacial capacitance. As shown in Figure 5, the permittivity of CaTiO₃ increases to a value of at least 55 between 10 and 30 nm thickness instead of 28 for an amorphous CaTiO₃ capacitor stack.⁵⁰ As depicted in Figure 5, the constant permittivity indicates a linear increase of crystallization with layer thickness. Therefore, this intermediate permittivity is not caused by an interfacial effect. Furthermore, the amount of crystallites does not change. For thicker samples, the measured permittivity increases to 105, and with this increase, the layer fully crystallizes. The inset of Figure 5 shows a typical capacitance voltage measurement of the 20 nm CaTiO₃ capacitor. The data follows a positive quadratic curvature with voltage, which is similar to measurements for amorphous CaTiO₃ capacitors. The dissipation factor D is below 0.01 in the measured voltage range, which proves the validity of the used Cp-D capacitance model.

In Figure 6, the corresponding leakage currents for CaTiO₃ layers with different layer thicknesses are plotted. Low leakage currents comparable to amorphous CaTiO₃ are shown for the samples between 15 nm (2 × 10⁻⁷ A/cm² at 1 V) and 30 nm (3.57 × 10⁻⁸ A/cm² at 1 V) layer thickness. These are extremely low values despite the presence of crystallites (even for stringent applications in DRAM capacitors). High leakage currents are measured, besides the 10 nm sample, for samples with a layer thickness above 30 nm even for low voltages, when crystallinity and permittivity increases. Trap assisted tunneling along numerous defect states at grain boundaries is suggested to be the major leakage mechanism. The strong increase in leakage current for the 10 nm sample can be attributed to the comparatively rough surface of the bottom electrode, as local field enhancement is stronger for thinner dielectrics.

![Figure 4](image4.png)  
Figure 4. HRTEM image of an embedded crystallite in a MIM capacitor stack with 5 nm oxide thickness. An oxide thickness series revealed an effective permittivity of approximately 55. The crystallization is not limited by the oxide thickness.

![Figure 5](image5.png)  
Figure 5. Permittivity of thickness series of CaTiO₃ capacitors deposited at 550 °C. For oxide layer thicknesses up to 30 nm, a permittivity of approximately 55 can be extracted due to a partially crystallized CaTiO₃ layer. For thicker layers above 30 nm, the permittivity and therefore the crystallinity of CaTiO₃ increase up to fully crystalline layers. (Inset) Capacitance voltage measurement of the capacitor with 20 nm CaTiO₃. A quadratic dependence of capacitance with voltage is visible.
agreement with the observations of Heitmann et al.\textsuperscript{55} in a crystallites are passivated by the amorphous matrix. This is in CaTiO\textsubscript{3}, the partially epitaxial growth does not result in the degree of structural order in the oxide. For thick layers of material system of Si/SiO\textsubscript{2}. When full layer crystallinity is reduction of leakage current compared to fully crystalline layers. In 10\textsuperscript{−30} nm thick layers, the permittivity of 55 is the result of a small number of crystallites with high permittivity embedded in the amorphous CaTiO\textsubscript{3} matrix with a smaller permittivity of 28. For different layer thicknesses, the constant permittivity of 55 implies a linear increase of crystallinity with increasing the oxide thickness to 30 nm. Distinct to fully crystalline layers, the leakage currents are comparable to those of amorphous samples. The degree of crystallinity is sketched in Figure 7, where the layer develops from isolated CaTiO\textsubscript{3} crystals (Figure 7b) to a fully crystallized CaTiO\textsubscript{3} stack (Figure 7a). This result strongly suggests that the grain boundaries as main leakage paths\textsuperscript{53,54} of the isolated crystallites are passivated by the amorphous matrix. This is in agreement with the observations of Heitmann et al.\textsuperscript{55} in a material system of Si/SiO\textsubscript{2}. When full layer crystallinity is present, significantly higher conductivity along grain boundaries (yellow sketched dotted paths in Figure 7b) occurs. As a result, with oxide thicknesses greater than 30 nm within the used deposition conditions, crystallinity, permittivity, and leakage current increase significantly.

5.2. Explanation of Reduced Leakage Current. The increase of crystallinity correlates well with the increase in leakage current for the thicker samples. In 10–30 nm thick layers, the permittivity of 55 is the result of a small number of crystallites with high permittivity embedded in the amorphous CaTiO\textsubscript{3} matrix with a smaller permittivity of 28. For different layer thicknesses, the constant permittivity of 55 implies a linear increase of crystallinity with increasing the oxide thickness to 30 nm. Distinct to fully crystalline layers, the leakage currents are comparable to those of amorphous samples. The degree of crystallinity is sketched in Figure 7, where the layer develops

Figure 7. Influence of ordered growth of CaTiO\textsubscript{3} in MIM capacitor stack. (a) The ordered growth does not change the conduction behavior for thick and fully crystalline layers. (b) For thin layers, the selective growth result in nanocrystallites embedded in an amorphous matrix. The grain boundaries are passivated (green) with a significant reduction of leakage current compared to fully crystalline layers.

Figure 8. Influence of ordered growth of CaTiO\textsubscript{3} on top of Pt compared to samples with unordered growth. Without ordering, the CaTiO\textsubscript{3} layer crystallization in thin layers is inhibited. Seeding crystals available from the substrate layer allow ordered growth of CaTiO\textsubscript{3} on top of some Pt facets.

5.2. Explanation of Reduced Leakage Current. The increase of crystallinity correlates well with the increase in leakage current for the thicker samples. In 10–30 nm thick layers, the permittivity of 55 is the result of a small number of crystallites with high permittivity embedded in the amorphous CaTiO\textsubscript{3} matrix with a smaller permittivity of 28. For different layer thicknesses, the constant permittivity of 55 implies a linear increase of crystallinity with increasing the oxide thickness to 30 nm. Distinct to fully crystalline layers, the leakage currents are comparable to those of amorphous samples. The degree of crystallinity is sketched in Figure 7, where the layer develops from isolated CaTiO\textsubscript{3} crystals (Figure 7b) to a fully crystallized CaTiO\textsubscript{3} stack (Figure 7a). This result strongly suggests that the grain boundaries as main leakage paths\textsuperscript{53,54} of the isolated crystallites are passivated by the amorphous matrix. This is in agreement with the observations of Heitmann et al.\textsuperscript{55} in a material system of Si/SiO\textsubscript{2}. When full layer crystallinity is present, significantly higher conductivity along grain boundaries (yellow sketched dotted paths in Figure 7b) occurs. As a result, with oxide thicknesses greater than 30 nm within the used deposition conditions, crystallinity, permittivity, and leakage current increase significantly.

6. DISCUSSION

Figure 8 summarizes the influence of the ordering substrate to the degree of structural order in the oxide. For thick layers of CaTiO\textsubscript{3}, the partially epitaxial growth does not result in a significant change of structural order, the layers are completely crystallized (top left and bottom left images). For thin layers, typically the crystallization is inhibited (top right image).\textsuperscript{56} The amorphous-to-polycrystalline phase transition can be described by classical nucleation theory according to Spinella et al.\textsuperscript{57} With the help of lattice matched substrate layers working as seeding crystals, the inhibition can be obviated. The polycrystalline Pt surface works as a seeding layer to reduce the forming energy of CaTiO\textsubscript{3} crystallites.

From simulations in literature, the \{111\} CaTiO\textsubscript{3} surface exhibits the largest surface energy. We believe this and the CaO\textsubscript{3}\textsuperscript{4−} terminated surface with the vacant oxygen atoms are responsible for the preferential growth on only the \{111\} terminated Pt surface. Obviously, the comparable lattice between Pt and CaTiO\textsubscript{3} should not result in any preferential growth on a specific Pt surface. As a result, the CaTiO\textsubscript{3} nanocrystallites specifically grow on \{111\} terminated Pt facets and are simultaneously passivated by the surrounding amorphous matrix (Figure 8, bottom right image).

According to Figure 8, the results were only measurable for ultrathin layers with inhibited layer crystallization. Further analysis is necessary to identify the reason for the preferential growth of CaTiO\textsubscript{3} only on the Pt \{111\} facets. In this study, we used the heterogeneous nucleation to grow embedded nanocrystallites of CaTiO\textsubscript{3} in a MIM capacitor stack. The nanocrystallites are passivated by the surrounding amorphous matrix, and as a final result, a reduction of leakage currents with an increased permittivity follows.

The presented results of CaTiO\textsubscript{3} as a model system for perovskites may allow preparing isolated crystallites with other materials of the perovskite group. These experiments can focus on the investigation of the amorphous–crystalline interface. We propose to investigate the influence of isolated and ordered crystallites of ferroelectric perovskites with commonly used sputtering techniques. For magnetic perovskites, the passivation may allow the investigation of switching behavior of isolated magnetic domains. Both systems will fill the gap between experiments on polycrystalline layers and isolated (ferroelectric or ferromagnetic) nanoparticles. All our embedded nano-crystallites exhibit the same crystal orientation; therefore, this layer growth results in an epitaxial-like behavior with industry standard sputter deposition technique.
The control and modification of the {111} Pt single crystal surface by, for example, ion beam bombardment can further allow the structured growth of 3D structures already passivated by an amorphous matrix. Thermal treatment of the Pt surface can be used to shift the favorable {111} surface facets to higher proportions.

7. CONCLUSION
The results presented in this work allow the search and investigation of samples with nanocrystallites surrounded by an amorphous matrix. Selected samples have been investigated with TEM to gain knowledge of the crystallinity for maximum permittivity of CaTiO3 in thin films. The reason for intermediate values of permittivity has been correlated to partially crystallized CaTiO3 layers. The formation of crystallites is substantially influenced by the Pt bottom electrode. There is a preferential growth of {111} CaTiO3 crystals on top of a Pt {111} surface resulting in isolated crystals in an otherwise amorphous matrix. This preferential growth does not benefit from good epitaxial relations of various crystal directions but from differences in surface energy of CaTiO3 contributing to the interface energy of the CaTiO3/Pt interface. Going to higher deposition/annealing temperatures and layer thicknesses, the layers become fully crystallized, and the preferentially oriented crystallites are overshadowed by the formation of unordered crystallites. The prepared layers exhibit an intermediate permittivity of 55 with low leakage currents comparable to currents in amorphous layers. This obviates the typical trade-off in application between full crystallinity and high permittivity on one hand and low leakage currents on the other hand for DRAM capacitor applications, for example.

ACKNOWLEDGMENTS
The authors want to thank the colleagues of Namlab for their support and Tina Sturm from the Leibniz Institute for Solid State and Materials Research Dresden (IFW Dresden) for several TEM sample preparations. Special thanks goes to Uwe Gaitzsch (IFW Dresden) to verify the Pt texture measurements. Also, Wytze Keuning (Eindhoven University of Technology) is acknowledged for TEM sample preparation using focused ion beam (FIB). The authors further want to thank R. Eglitis, H. S. Leipner and J. Heitmann for fruitful discussions and J. Dshemuchadse (ETH Zürich) for the crystal building.

REFERENCES