# Local structure and point-defect dependant selective atomic layer deposition of copper(I) oxide and metallic copper thin films

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Area-selective atomic layer deposition has attracted much attention in recent years due the possibility of achieving accurate patterning with nanoscale precision, even for 2D and 3D nanostructures, which renders the technique compatible with the continuous trend to miniaturization in the electronic industry [1]. In most cases, the area-selective growth is achieved by deactivation of part of the substrate with the use of self-assembly monolayers (SAMs), previous to atomic layer deposition (ALD), resulting in the localized growth of the desired material in restricted areas of the substrate [2]. However, the use of SAMs is no without challenges, since they are not always compatible with high-temperature thermal ALD, plasma-assisted ALD or ozone-based ALD processes [1]. Here, we present a different approach to achieve an area-selective ALD (AS-ALD) process that is based on the modulation of the substrate properties to achieve simultaneous localized growth of different materials on different regions of the substrate. In particular, we will demonstrate the area-selective deposition of $Cu_2O$ and metallic Cu thin films on ZnO substrates [3]. The modulation of the ZnO properties is achieved by varying the ZnO conductivity/point defect density in a wide range ($10^{-4}$ to $10^{3}$ S/cm) by tuning the oxygen partial pressure in the sputtering chamber, which influences the final material deposited by ALD: $Cu_2O$ or metallic Cu. The selectivity is obtained here thanks to the intrinsic selectivity of the Cu-precursor employed toward the different ZnO surfaces of different conductivities/ point defect densities. Therefore, the process is simpler than other patterning approaches since it doesn't require the use of inhibitor or blocking molecules to prevent local growth.

A temperature-driven and conductivity-driven selective deposition processes was verified on ZnO, and Al-doped ZnO (AZO) substrates, as is shown in Figure 1 a. Higher temperatures favor the reduction of Cu into the precursor from $Cu^{2+}$ to metallic $Cu^{0}$, and this is the reason why at 300°C, the window for deposition of $Cu_2O$ becomes smaller, and metallic Cu is obtained even for low-conductive substrates. In contrast, at lower temperature, the reduction of $Cu^{2+}$ into $Cu^{1+}$, to form $Cu_2O$, is extended to more conductive substrates (see schematic in Figure 1 b). In addition to temperature and substrate conductivity, in the case of $Cu_2O$, the orientation relationship between the film and the substrate seems to play also an important role on the selective growth, and $Cu_2O$ easily grows epitaxially on (001) ZnO with [110] $Cu_2O$ || [001] ZnO films.

As a proof of concept a bi-layer structure was fabricated composed of highly-conductive AZO regions and low-conductive ZnO areas. An AS-ALD process was demonstrated by high resolution TEM and electron energy loss spectroscopy, where the $Cu_2O$ films was deposited on the low-conductive ZnO regions and metallic Cu on the highly-conductive AZO areas (see Figure 2 a). Based on the AS-ALD process, $Cu_2O$/ZnO/AZO nanojunctions were successfully fabricated. I-V characteristics of the nanojunctions, measured by conductive atomic force microscopy, show a non-linear rectifying behavior typical of a p-n junction (see Figure 2 b), which is promising for low-cost all-oxide transparent microelectronics and photovoltaics.

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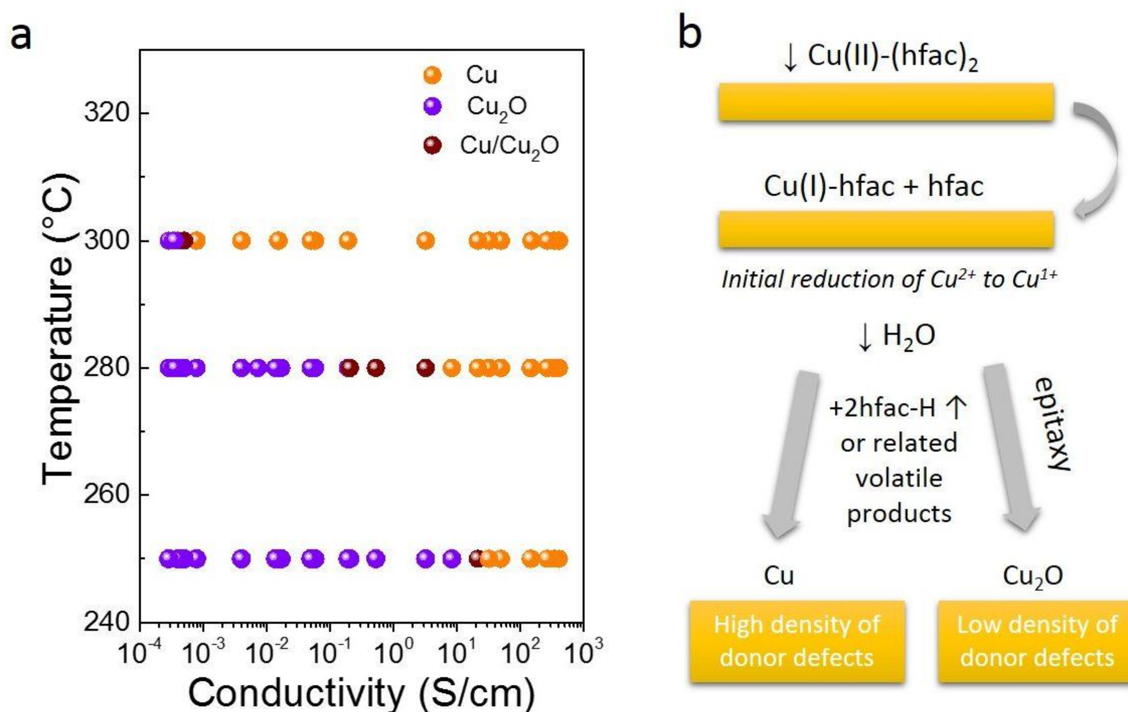


**Figure 1**. Phase diagram of the different materials (Cu, $Cu_2O$ or a mixture) deposited by ALD depending on the temperature and substrate conductivity (left). Schematic of the AS-ALD mechanism on ZnO substrates (right).

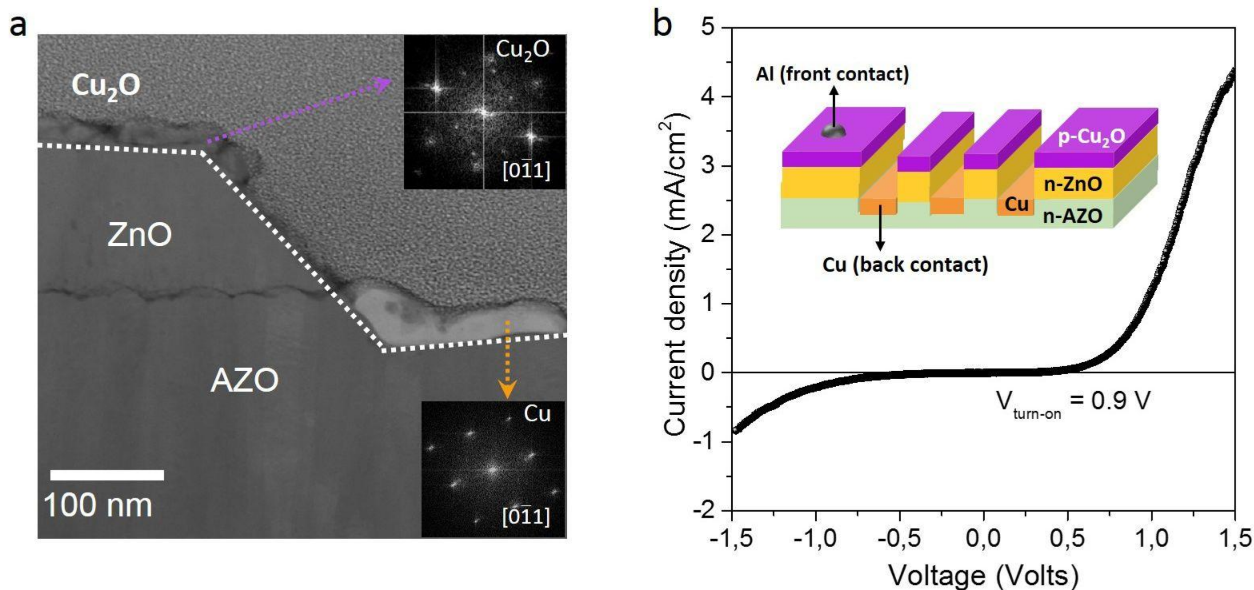


**Figure 2**. Cross-section TEM micrograph of the ZnO/AZO bi-layer after the AS-ALD of $Cu_2O$ and metallic Cu (a). Current density – voltage characteristics of the nanojunctions, the schematic of the sample configuration is shown as inset (b).

# Inherent substrate-selective atomic layer deposition of polycrystalline gallium nitride

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**Introduction:** Gallium nitride (GaN), one of the group III-Nitride semiconductors, has received much attention due to its wide and direct bandgap, high electron mobility and high breakdown field[1], allowing to realize light emitting diodes, high electron mobility transistors, etc.[2] In integrated circuits (IC) technology, GaN has been classically used in its monocrystalline form, showing the best performance. In comparison, polycrystalline (poly-) GaN has not been much explored, although the number of applications of poly-GaN in electronic devices[3-4] is growing.

**State-of-the-art:** The previous reports on atomic layer deposition (ALD) of poly-GaN with the industrially-relevant precursors such as trimethylgallium (TMG) and ammonia ($NH_3$)[5-6] have resorted to additional means of activation, e.g., by plasma. Plasma was essential to dissociate $NH_3$ into radicals, thereby realizing the GaN ALD at low temperatures (*T*). Since $NH_3$ is chemically stable at $T$<600 $^oC$[7] and TMG already starts dissociating at $T$>150 $^oC$[8], enabling self-limiting surface reactions for ALD from TMG and $NH_3$ requires the assistance of radicals, which can be produced by plasma. Otherwise, the growth rate at $T$<400 $^oC$ is extremely low; higher temperatures cause heavy Ga- and C-contamination in the layers[9].

Recently, based on the existing mechanism of thermal ALD of aluminum nitride (AlN) films[12], we proposed and realized a similar chemical pathway to facilitate low temperature (~400 $^oC$) poly-GaN ALD from TMG and $NH_3$, even without radical assistance[10-11]. The GaN growth occurred through two stages : (i) formation of TMG:$NH_3$ 'surface adduct' complex, and (ii) conversion of this complex into Ga–$NH_2$–Ga linkage, signifying a unit of GaN. Similar to AlN, the GaN pathway implies –$NH_2$-termination of the film surface after each $NH_3$ pulse. The presence or absence of –$NH_2$-terminations is hypothesized to inherently facilitate substrate-selective ALD of poly-GaN.

**This work:** We utilized in-situ spectroscopic ellipsometry to monitor the thickness evolution in real-time, focusing on the initial growth (or incubation time*) in the GaN ALD. Different substrates, such as H-terminated Si(111), OH-terminated $SiO_2$, and –$NH_2$-terminated AlN and GaN, were explored in terms of the incubation time. While the H- and OH-terminations increased the incubation (140 cycles on both Si and $SiO_2$, see Fig. 1-left), the–$NH_2$-terminations on the in-situ deposited AlN and GaN seed-layers dramatically reduced it to 20 cycles, for both. Such differences in the incubation time may facilitate area-selective ALD.

On the contrary, plasma-assisted ALD of GaN (with TMG and $NH_3$–Ar plasma) does not offer substrate-dependent incubation. On both Si and $SiO_2$ substrates, it is only 25 cycles (Fig. 1-right), i.e. similar to that on the $NH_2$-terminated AlN and GaN seed-layers. This implies that the plasma-generated radicals ($NH_x$, x=2-0) furnish both Si and $SiO_2$ with the terminations required to readily achieve the GaN growth. Providing $NH_2$-terminations by in-situ pre-annealing of $SiO_2$ in $NH_3$ (instead of the $NH_3$ plasma) also reduces the incubation phase from 140 to 80 cycles (Fig. 1-right).

The ultimate goal is to achieve selective ALD of GaN on the *same* substrate, e.g., on AlN or $SiN_4$ surfaces on Si (or $SiO_2$) substrates. This implies ex-situ patterning by lithography and etching, requiring an exposure to air. At present, ex-situ patterning of AlN results in long incubation times (Fig. 2-left), similar to that observed on Si and $SiO_2$ before (compare to Fig. 1-left). The air-exposure and the subsequent treatment presumably oxidize the original –$NH_2$-terminations on AlN. To achieve the selectivity, it is important to in-situ restore them. However, patterning a CVD-$Si_3N_4$ layer (Fig.

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*defined here as the number of ALD cycles required to grow 1 nm GaN film.

2-right, showing the schematic) leads to much longer incubation time (Fig. 2-left). It is favorable for achieving selective ALD on $Si_3N_4/SiO_2$, $Si_3N_4/Si$ and $Si_3N_4/AlN/SiO_2/Si$ material combinations.

In our presentation, we will discuss the mechanism of the radical-free ALD of poly-GaN layers at 400 ºC, emphasizing on the results of the substrate-selective ALD.

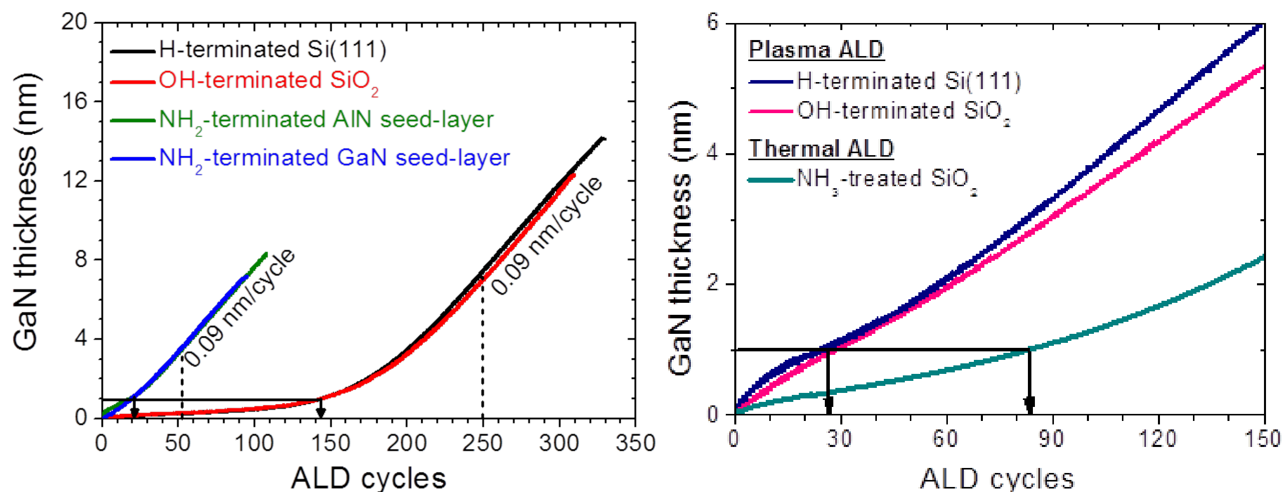


**Figure 1**. Thickness evolution of GaN layers on different substrates during thermal ALD, monitored by in-situ spectroscopic ellipsometry (SE). **Left** – thermal ALD on H-terminated Si(111) and OH-terminated $SiO_2$ leads to an incubation of 140 cycles, whereas –$NH_2$-terminated AlN and GaN seed-layers reduce the incubation to 20 cycles. Beyond 250 cycles on Si(111) and $SiO_2$, and 50 cycles on AlN and GaN, the growth per cycle stabilizes at 0.09 nm/cycle. **Right** – Plasma-enhanced ALD of GaN on H-terminated Si(111) and OH-terminated $SiO_2$ results in the same incubation of 25 cycles, whereas thermal ALD on $NH_3$-annealed $SiO_2$ substrate (600 ºC, 45 min) shows a reduction from 140 to 80 cycles.

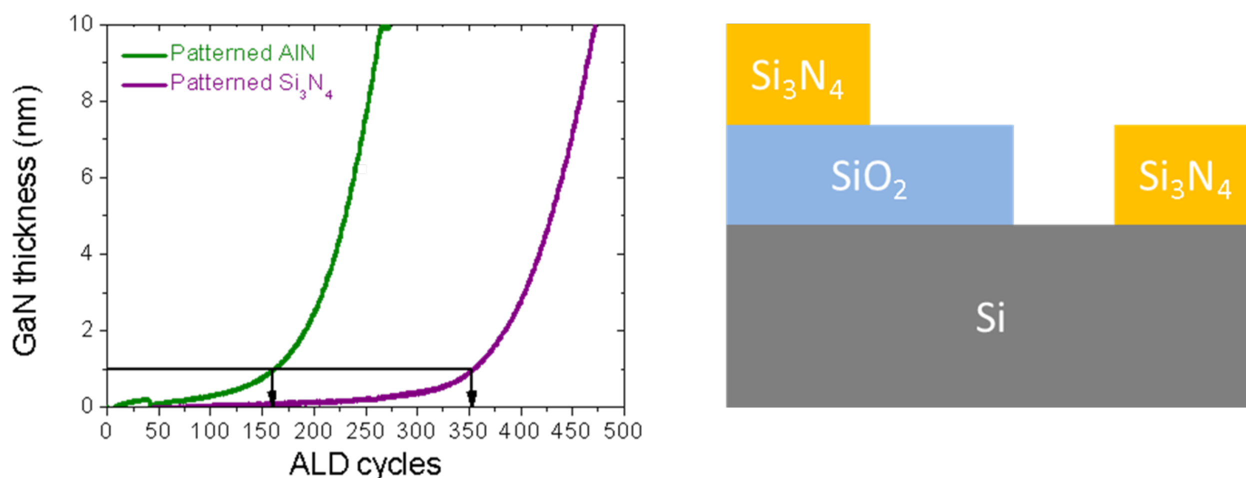


**Figure 2**. **Left** – Comparison of GaN growth during thermal ALD, on ex-situ patterned AlN and $Si_3N_4$ surfaces. The patterned AlN exhibits similar incubation as on Si and $SiO_2$ substrates, but the difference with $Si_3N_4$ is noticeable. **Right** – Schematic of an ex-situ patterned $Si_3N_4/SiO_2/Si$ material combination.


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# MOCVD process design for luminescent rare-earth sulfides circumventing $H_2S$ as co-reactant

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Rare-earth sulfides (RES) such as $Nd_2S_3$, $Gd_2S_3$ or EuS possess fascinating functional properties rendering them very attractive for implementation in a broad range of applications including optics and electronics.[1] However, literature reports on research related to RES in thin film form are scarce and especially their growth *via* vapor phase deposition routes such as metalorganic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD) has hardly been explored although these techniques have a huge potential for large scale applications. One factor for the slow progress in this area of research could be the lack of suitable RE precursors.

For the CVD of RES, the high oxophilicity of the RE metals promotes parasitic growth of rare-earth oxides and oxysulfide species. This suggests an exclusion of oxygen in the ligand sphere of the RE complexes ruling out common ligand systems such as beta-diketonates (acac, thd). This prompted us to employ the all-nitrogen bonded class of RE amidinates and guanidinates as precursors which comprise beneficial thermal characteristics combined with a high reactivity. Although these precursors were already tested successfully for a range of materials such as rare-earth oxides and nitrides yielding high quality thin films[2], their application for RES was not explored. Thus, our focus was to develop new processes for RES using the amidinate and guanidinate class of precursor under moderate process conditions including the choice of the co-reactants which is a crucial parameter. Generally, toxic hydrogen sulfide ($H_2S$) gas is implemented in developing RES *via* vapor phase routes to ensure a sufficient reactivity towards the applied precursors. Due to the pronounced reactivity of the newly developed Nd guanidinate and amidinate precursors, we were able to circumvent $H_2S$ employing commercially available, non-toxic elemental sulfur ($S_8$).[2]

Herein, we present a facile process for the growth of luminescent $Nd_2S_3$ thin films *via* MOCVD at moderate process conditions using two new precursors neodymium guanidinate [$Nd(dpdmg)_3$] and neodymium amidinate [$Nd(dpamd)_3$], depicted in Figure 1. The compounds were analyzed by means of single-crystal X-ray diffraction, $^1H$ nuclear magnetic resonance spectroscopy and elemental analysis. For the evaluation of the thermal properties and fragmentation behavior, thermogravimetric analysis and mass spectrometry were carried out. Both precursors were implemented in a sulfide MOCVD process in a substrate temperature range of 400 °C to 600 °C using just evaporated elemental sulfur as co-reactant yielding high purity $\gamma$-$Nd_2S_3$ which were thoroughly characterized in terms of structure (X-ray diffraction), composition (Rutherford backscattering spectrometry, X-ray photoelectron spectroscopy) and morphology (scanning electron microscopy, Figure 2). For the functional properties, UV-Vis spectroscopy and photoluminescence measurements were performed showing that the as-deposited $\gamma$-$Nd_2S_3$ thin films exhibit luminescent properties with the optical bandgap ranging from 2.3 eV to 2.5 eV. This is the first illustration on the growth of $Nd_2S_3$ via MOCVD routes and is very promising.[2] The new process circumvents post-deposition treatments such as sulfurization to fabricate the desired $Nd_2S_3$, which paves the way for large scale synthesis and opens up new avenues for exploring the potential of this class of materials with properties for functional applications.

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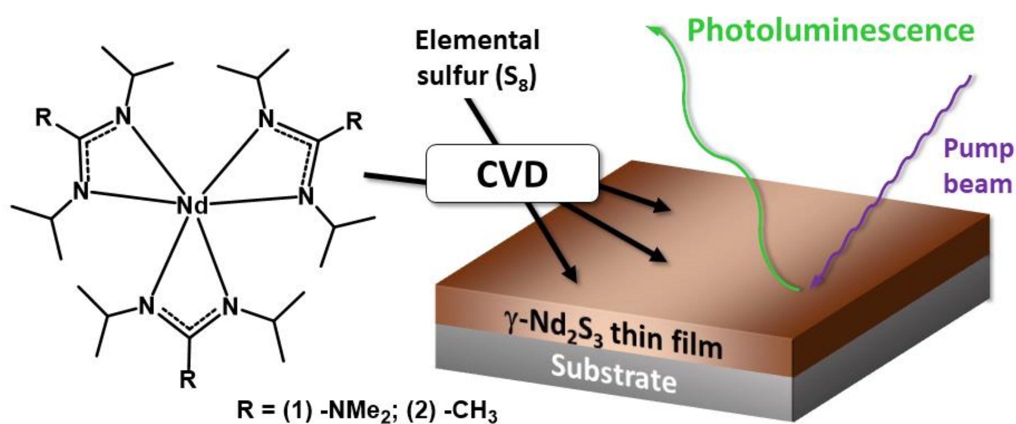


**Figure 1**: Molecular structure of the precursors [Nd(dpdmg)$_3$] **1** and [Nd(dpamd)$_3$] **2** applied in an CVD process with elemental sulphur ($S_8$) as co-reactant. The photoluminescence measurement is illustrated with the colored arrows.

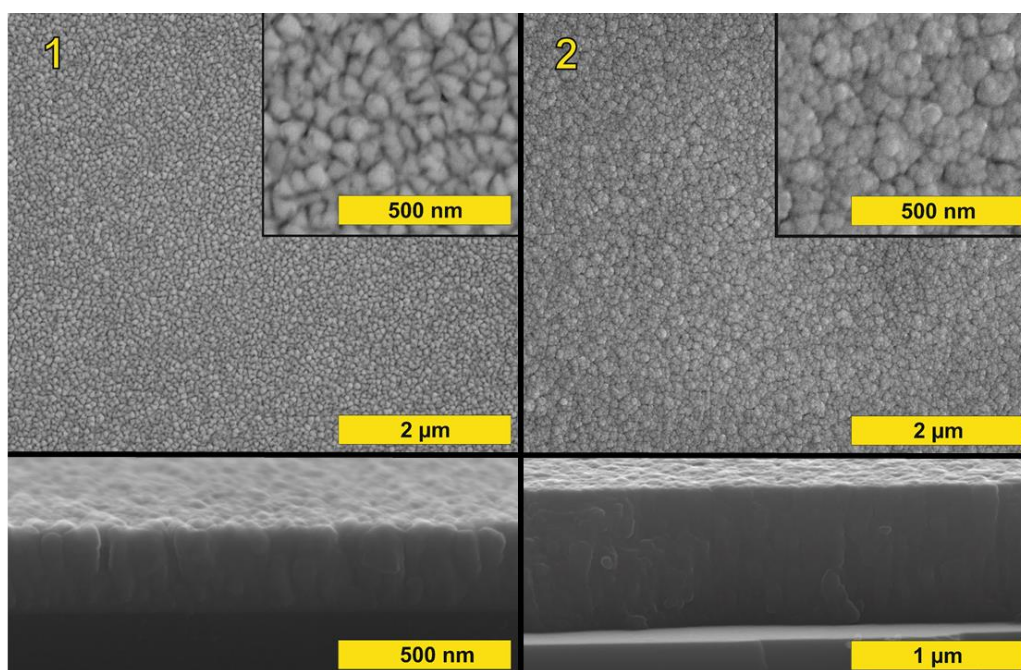


**Figure 2**: SEM images of $Nd_2S_3$ on Si(100) substrates grown from Nd(dpdmg)$_3$] **1** and [Nd(dpamd)$_3$] **2** at 500 °C. The upper micrographs show the top-view with increased magnification in the inset, while the lower images present the cross-sectional view.