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Epitaxial Growth of Thin Films

Daniel Rasic and Jagdish Narayan

Abstract

Epitaxial thin film heterostructures are critical for integrating multi-functionality on a chip and creating smart structures for next-generation solid-state devices. Here, we discuss the traditional lattice matching epitaxy (LME) for small lattice misfit and domain matching epitaxy (DME), which handles epitaxial growth across the misfit scale, where lattice misfit strain is predominant and can be relaxed completely, meaning that only the thermal and defect strains remain upon cooling. In low misfit systems, all three sources contribute to the residual strain upon cooling, as result of incomplete lattice relaxation. In the second part of the chapter, we will discuss the two critical contributors to the stress of the epitaxial film: the thermal coefficient of expansion mismatch and the lattice plane misfit. In the last part of the chapter, we will focus on unique cases where room temperature epitaxial growth is possible in nitride and oxide thin films.

Keywords: thin films, annealing, defects, epitaxy, lattice misfit

1. Introduction

The modern civilization operates in bits (zeroes and ones), and the start of the “binary” (digital) era was made possible by the invention of transistor in 1947. Since then, the improvements were growing at exponential rate by halving the size of each transistor and doubling the processing speed each year (a.k.a. Moore’s law) [1]. The fundamental template on which transistors are made is silicon. Experimentally, the modern transistors are made using thin-film growth technologies. With each size decrease, new scaling issues occurred primarily because of deposition technology limitations of that era. However, as we move closer to single nanometer nodes, fundamental limitations that originate from material properties start to take over as the main challenges that were previously reserved for instrumentation [2, 3].

In this chapter, the overview of thin-film growth is provided, followed by the discussion on epitaxy and lattice misfit considerations. Finally, the role of temperature in film growth is discussed with some examples.

1.1 Pulsed laser deposition

One of the most versatile and powerful growth methods used in thin-film growth used today is pulsed laser deposition (PLD). Main advantages over sputtering, physical vapor deposition (PVD), chemical vapor deposition (CVD) and other techniques is its forward-directed, non-equilibrium growth of multi-layered novel and exciting materials that preserve the target stoichiometry at much lower temperatures [4–7].

Perhaps the main advantage of the PLD process is the ability to deposit several multi-component materials in-situ with stoichiometry preserved [7]; an impossible feat with equilibrium methods. In **Figure 1**, a schematic of a PLD assembly is shown. The high-energy pulsed laser is used to ablate the target and form a plasma-like plume that deposits target material on the substrate of choice. The number of laser pulses during growth dictates the thickness of the film, and rotating the target assembly allows for multi-layer growth. In PLD, the energy of the ablated species is ~ 16 eV, compared to the energy of the ejected species in electron and thermal beam evaporation techniques (e.g. thermal energy, kT at 1200 K is ~ 0.1 eV). The high-energy of deposited species lowers the overall thermal budget requirement for epitaxial growth by providing enhanced mobility and growth on the substrates [8].

Epitaxy describes the oriented growth of a crystalline material on top of another. In a more specific term, it describes, predominately, the thin-film growth of a material on a substrate with a well-defined relationship. In the case of substrate/film growth, the film and the substrate have different chemistry, crystallographic properties and expansion coefficients. Therefore, most substrate/film combinations will not yield epitaxial films. The most obvious, first-order consideration to determine the probability of epitaxial growth in substrate/film growth is by calculating the lattice misfit at the interface by

$$\epsilon_m(\%) = \left(1 - \frac{d_f}{d_s}\right) \times 100 \quad (1)$$

where d_f and d_s are lattice plane spacing in the in-plane directions between the film and the substrate, respectively.

Epitaxial thin film growth is almost always preferred over textured (single fixed axis alignment between substrate and film) or polycrystalline growth because the physical properties; e.g. conductivity can be enhanced and controlled [9]. Epitaxial thin films also need considerably smaller amounts of material to achieve performance comparable to randomly oriented (polycrystalline or nanocrystalline) films, which becomes an important consideration when using toxic or rare materials.

1.2 Lattice matching epitaxy

When the lattice misfit is small ($7\% > \epsilon_m > 0\%$), the film growth occurs with one-to-one matching of lattice planes. Due to the difference in the lattice constants, lattice

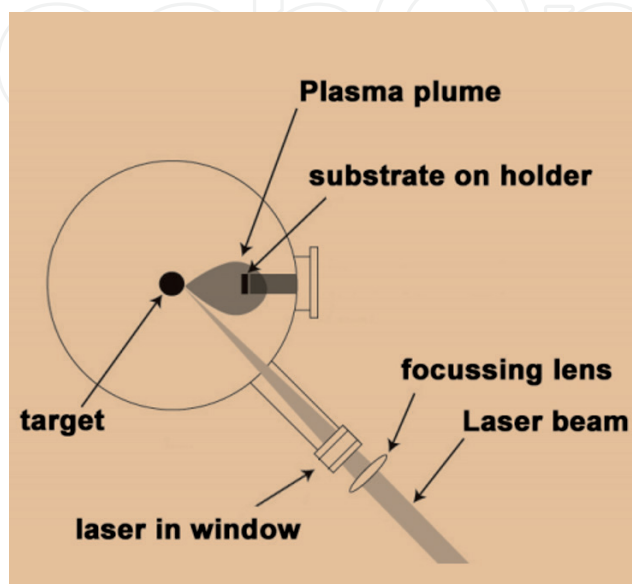


Figure 1.
Sketch showing the pulsed laser deposition assembly.

strain in the film is created that increases with film thickness. The accumulated strain is subsequently relaxed, at a certain thickness, by dislocation nucleation on the surface and propagation to the interface of the film and the substrate. The thickness at which this occurs is called the critical thickness of the film and is dictated by the lattice misfit, nucleation energy of dislocation and available slip systems as determined by the Schmidt factor. This means that the critical thickness is inversely correlated to the lattice misfit, i.e. the larger lattice misfit will cause relaxation via dislocations at a smaller film thickness.

1.3 Domain matching epitaxy

It was shown in recent times that the traditional lattice matching epitaxy (LME) is not able to explain the growth of several substrate/film heterostructures. For example, epitaxial titanium nitride thin films were grown on silicon by Narayan et al. as shown in **Figure 2** [10]. In the mentioned case, the lattice misfit is ~22.5%, suggesting that the lattice strain that is created on the film by the substrate would cause an immediate dislocation at the first step of film growth. To address this large misfit epitaxial thin film growth, the concept of domain-matching epitaxy (DME) was introduced that provides a universal paradigm for thin film epitaxy across the misfit scale [11]. The DME paradigm is centered around matching of integral multiples of lattice planes while the misfit in-between the integral multiples is relieved by the principle of domain variation, where alternation of domains occurs with a certain frequency to accommodate the misfit.

Theoretically, if the misfit yields the perfect matching ratios of planes ($md_f = nd_s$), the residual strain will be zero. Contrastingly, if the misfit yields non-zero residual strain, it is alleviated by two domains, alternating with a certain frequency (α) to minimize the residual strain, given as

$$(m + \alpha) d_f = (n + \alpha) d_s \tag{2}$$

where α is the domain variation (frequency) parameter. For example, if $\alpha = 0.5$, then m/n and $(m + 1)/(n + 1)$ domains alternate with the same frequency [11]. With

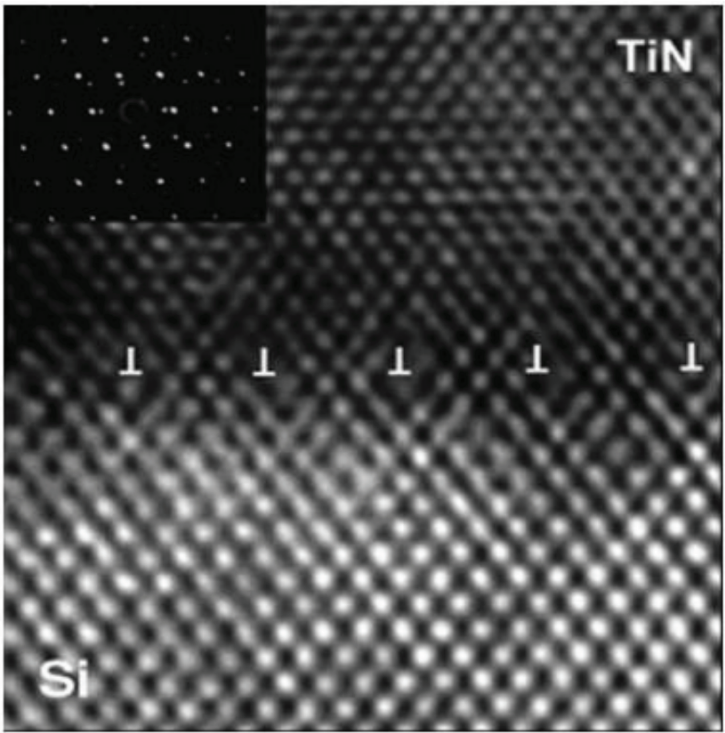


Figure 2.
HRTEM image of TiN/Si(1 0 0) interface with alternating 4/3 and 5/4 domains [10].

additional research, it was shown that epitaxial growth is possible for many film/substrate systems such as AlN/Al₂O₃, TiN/Al₂O₃, ZnO/Al₂O₃, MgO/Al₂O₃, MgO/STO, LSMO/MgO, MgO/Si, STO/Si, etc. [11, 12]. The two critical steps in the kinetics of thin film relaxation and growth are dislocation nucleation and subsequent propagation. Firstly, nucleation of dislocations occurs at the free surface, and the nucleation barrier is determined by the presence of surface steps. Experimentally, it was demonstrated that the nucleation of dislocations is lower when the film is under compressive stress as opposed to tensile stress [13]. This concept can be applied in the case of Si/Ge system where the critical thickness is found to be larger for films under tensile stress than in the Ge/Si system where the film is under compressive stress. Taking the misfit strain into consideration, three cases can be considered in epitaxial film growth: large ($>10\%$), intermediate ($2\% < x < 10\%$) and small ($<2\%$).

1. In the case of large planar misfit strains ($\geq 10\%$), the critical thickness is less than a monolayer and therefore, the film grows fully relaxed at growth temperatures with very little residual strain as all of the strains (lattice misfit, thermal misfit and defects) are additive. With subsequent cooling, only thermal and defect strains remain, and the cooling rate plays a critical role in trapping defects associated strains and influencing the dislocation nucleation and propagation.
2. In the case when the planar misfit strains are intermediate, the thickness of the film before dislocations form is several monolayers. Dislocations determine the residual strains, however, if the lattice misfit strains are not relaxed, they will dominate the total residual strain (the contribution from thermal strains is in the order of 0.1–0.2%).
3. When the interplanar misfit strain is small, the pseudomorphic growth can occur, where the film adopts the interplanar spacing of the substrate. As the thickness of the pseudomorphic layer increases, strain-free energy accumulates and, above the critical thickness, it forbids uniform growth and a novel equilibrium structure can sometimes form. In this case, the strain-free energy competes with the chemical free-energy of the metastable pseudomorphic phase to limit the critical thickness [11]. This novel phase can have no residual strain, with misfit dislocations serving as a strain buffer between the pseudomorphic transition layer and a newly formed phase. In this case, the critical thickness is within the order of magnitude of the interplanar spacing due to the large misfit between the new phase and the pseudomorphic transition layer. These pseudomorphic structures have been reported in TiO₂/Ti₂O₃/Al₂O₃ and VO₂/V₂O₃/Al₂O₃ heterostructures, which follow the planar matching domain epitaxy paradigm [14].

2. Thermal misfit considerations

For a high-quality, epitaxial thin-film growth, the deposition techniques generally required high temperatures and strictly controlled environment [15, 16]. Little consideration was given to parameters such as dislocation formation energy, diffusion and bonding energy. Laws of thermodynamics put limits on what growth conditions are possible, and with high-temperature deposition, the overall process preserves the equilibrium. Thermal misfit strain arises as a result of different coefficients of thermal expansion between the substrate and the film. Thermal misfit strain (ϵ_T) in the film plane is given by

$$\epsilon_T = (\alpha_{\text{Substrate}} - \alpha_{\text{film}}) \Delta T \quad (3)$$

For example, if the expansion coefficient of the film is larger than that of the substrate, the film will have tensile stress upon cooldown and the substrate will experience compressive stress subsequently.

In case of strongly bonded oxide and nitrides, where dislocation formation and propagation steps are difficult, the thermal misfit stress gets more prominent. With increasing the thickness of the film, the strain in the film accumulates and causes cracking and delamination.

3. Thermal processing of thin film heterostructures

As discussed earlier in this chapter, the quality of thin film growth is mainly influenced by lattice misfit and thermal coefficient of expansion coefficient. Considering both factors is the first step toward creating a high-quality, epitaxial interface. Combining the results from literature, three distinct growth categories were proposed by Rasic and Narayan: (i) non-epitaxial samples, (ii) epitaxial films grown on small misfit substrates (LME) and (iii) epitaxial films grown on large misfit substrates (DME) [17]. In the following, a summary of the critical considerations for epitaxy across the misfit scale in the presence of lattice/planar misfit, thermal and defect strains is presented. In order to establish each category, a set of three epitaxial (110) films of lanthanum strontium manganese oxide (LSMO) grown with orders of magnitude different oxygen partial pressure conditions were subjected to annealing experiments [17]. The findings indicated that annealing above growth temperature ($\sim 900^\circ\text{C}$) created an irreversible strain relaxation in the films which degraded the magnetization saturation of LSMO films. The hypothesis was further supported by an in-situ XRD experiment that showed a near-linear increase in interplanar spacing (d) until $\sim 690^\circ\text{C}$ for MgO and $\sim 520^\circ\text{C}$ for LSMO layer. Additional increase in the temperature indicated a decrease in the unit cell size of the film and the buffer layer, suggesting that the samples were subjected to both irreversible defect nucleation and recombination, and reduction of oxygen. Partial recovery of magnetic properties was seen with samples being subsequently annealed in pure (99.99999%) oxygen at 700°C for approximately 6 hours. This is assumed to be due to the improved stoichiometry, grain growth and defect annihilation. Nevertheless, XRD showed that characteristic Bragg peaks of the film never returned to the starting value, suggesting that the irreversible process occurred with the high-temperature (900°C) air annealing. Similar thermal experiments in high-vacuum instead of atmosphere were conducted and results indicated a complete collapse of the perovskite crystal structure in the LSMO films suggestive of the significant reduction. Lastly, lower temperature ($\sim 500^\circ\text{C}$) oxidation experiment was conducted (**Figure 3**) on the as-grown sample that resulted in no observable change in the unit cell size, suggesting that the strain state of the film remained constant [17].

From literature, substantial research has been reported on various annealing treatments of LSMO thin films [18–27]. However, correlation between the measured physical properties and structural changes has been elusive. Therefore, It was proposed that the role of annealing treatments on LSMO films can be categorized into three (3) discrete groups: (i) non-epitaxial samples (e.g. nano-crystalline and polycrystalline thin films, and bulk samples), (ii) small lattice misfit epitaxial

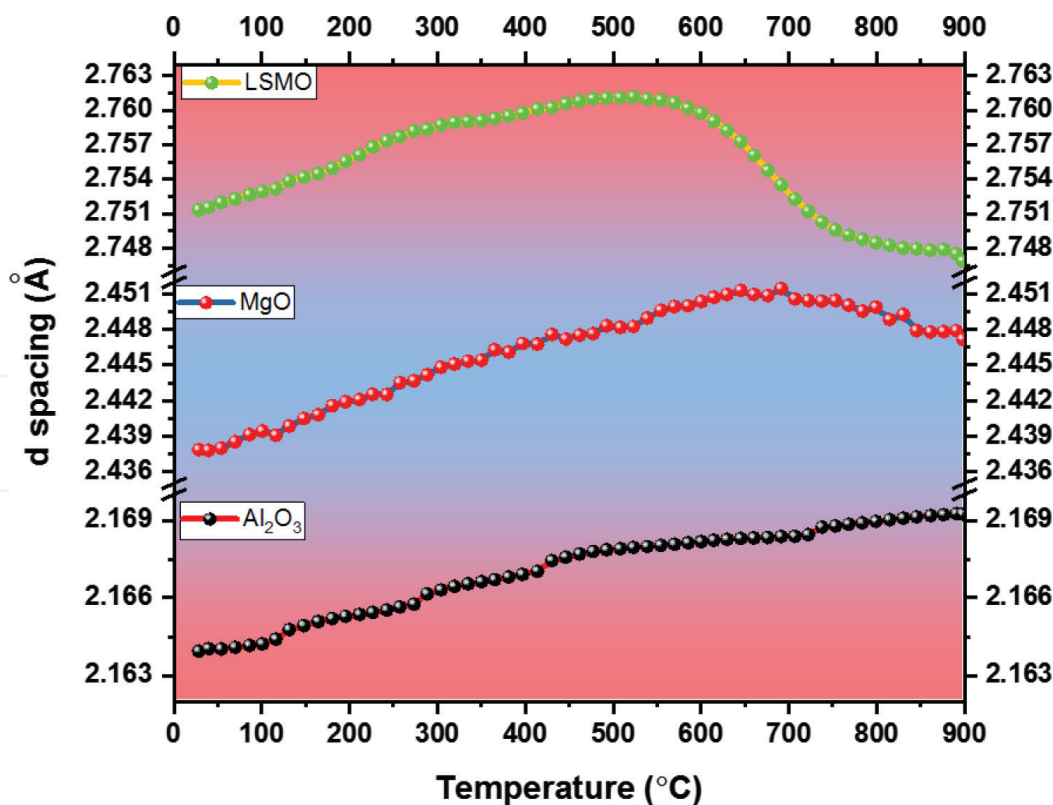


Figure 3.

In-situ X-ray diffraction scan (XRD) showing the change in the interplanar spacing (d) of the (110) LSMO, (111) MgO and (0006) Al₂O₃ Bragg peaks with respect to changing temperature. At ~520°C (LSMO) and ~690°C (MgO) the drop in d spacing is observed, indicating the strain relaxation and oxygen reduction [17].

heterostructures (e.g. STO/LSMO structure) grown by the traditional lattice-matching-epitaxy (LME), and (iii) epitaxial heterostructures grown by the principle of domain matching epitaxy (DME) with a large (>7%) lattice misfit between the film and substrate.

- i. In the first (i) category (non-epitaxial samples), high-temperature annealing expectedly increases the grain size, causes defect recombination and annihilation that improves physical properties such as magnetization saturation. Strain relaxation mechanism by dislocations is not present as there is no significant epitaxial relationship between the substrate and the film causing grain growth to be the dominant effect during heat treatments [18, 28].
- ii. In small lattice misfit (<7%) substrate/film heterostructures grown by LME (e.g. SrTiO₃, LaAlO₃ and BaTiO₃), the unrelaxed residual lattice misfit strain accumulates with increasing film thickness until the critical thickness where dislocation nucleation and formation starts relaxing the structure [11]. For example, the critical thickness is ~55 nm in the STO/LSMO system [29]. In this example, the film thickness becomes an additional parameter.
 - (iia) When films are grown with small lattice misfit below the critical thickness value, the total strain that the structure experiences is accumulating and adding to the residual thermal strain.
 - (iib) When the same heterostructure is grown above the critical thickness, the heterostructure behaves similarly to the large lattice misfit samples (iii), meaning that the residual lattice misfit strain is marginal and the main

contribution to the strain is from the mismatch of expansion coefficients between the substrate and the film.

In (iia) and (iib), the subsequent thermal annealing below the growth temperature does not result in a noticeable strain relaxation. Consequently, LSMO films annealed in either oxygen [22] or air [20] did not show significant improvements in magnetic properties. In these cases, the thermal expansion coefficients of the STO ($\sim 1.11 \times 10^{-5} \text{ K}^{-1}$) [30] and LSMO ($\sim 1.16 \times 10^{-5} \text{ K}^{-1}$) [31] are comparable, resulting in a small change of the overall strain state with temperature. This means that for the small lattice misfit films grown below the critical thickness (iia), the behavior is similar to that of large lattice misfit systems annealed below the growth temperatures (iiia) and the non-epitaxial samples (i). Furthermore, for the small lattice misfit heterostructures grown above the critical thickness (iib), the film will behave similarly to the large lattice misfit epitaxial films that were annealed above the growth temperature (iiib): both systems will relax via dislocation formation [32]. Following enhancement of the physical properties by thermal treatments is due to grain growth and decrease of oxygen vacancies in the film.

iii. The epitaxial thin-film growth dynamic changes significantly with a large lattice misfit systems ($>7\%$) and is explained by domain matching epitaxy paradigm (DME), which predicts strain relaxation via dislocation formation at the substrate/film interface. Firstly, an equilibrium number of dislocations and point defects is present to cancel the lattice misfit strains at the growth temperature. After the deposition of the film, the lattice misfit plays no role in the relaxation mechanism. Instead, the thermal expansion mismatch dictates the residual strain in the film. Hence, the behavior of the film that is undergoing thermal annealing is controlled by the temperature at which the process is occurring and therefore, two independent behaviors are reported.

(iiia) In the case where the sample is subjected to thermal annealing below the original growth temperature, there is no change in the strain state of the sample as all the dislocations remain at the interface and improvements in the physical properties and structure are due to grain growth and point defect annihilation. This behavior is similar to samples in category (i) in the entire temperature range, and category (ii) below the growth temperature.

(iiib) Finally, when annealing the large lattice misfit heterostructure above the original growth temperature, the strain state of the film is “recalculated”. In other words, additional formation of dislocation occurs that changes the strain landscape in the film and at the interface. In this case, additional consideration needs to be taken regarding the pressure and composition of the gas in the environment. In the experiments by Rasic and Narayan, the formation of dislocations and film reduction were mutually inclusive at high-temperature thermal processing.

4. Room-temperature epitaxial thin film growth

Reducing the thermal budget of epitaxial thin film growth has been one of the biggest challenges for the electronics industry. By using the pulsed laser deposition technique and starving the system of thermal energy, epitaxial growth is made possible at room temperatures [8]. The ability to use a lower energy budget for epitaxial thin film growth is not only interesting from a cost saving perspective, but also from the diffusion considerations. The semiconductor industry is interested

in finding a solution to prevent the electron tunneling phenomena that occurs in a doped silicon once the feature size becomes smaller than 5 nm. Lowering the temperature at which the devices are made will decrease the interfacial diffusion between the functional layers and allow for better performance. The temperature dictates the kinetics and energetics of film growth. Therefore, as a general rule, reducing the thermal budget increases the defect concentration and destroys the epitaxy of the thin films [33–35]. On the other hand, it also decreases the overall cost of fabrication significantly. For these reasons, room temperature growth of high-quality epitaxial thin films that possess minimal viable product characteristics would revolutionize the industry.

In this part of the chapter, a successful room temperature, epitaxial growth of titanium nitride on c-cut (0001) sapphire is reported. The growth is governed by the principle of domain matching epitaxy (DME) where the lattice misfit is $\sim 8.46\%$. DME theoretical framework was used in this paper to explain the experimental growth. Films were grown at 650°C, 450°C and room temperature (RT). Higher residual out-of-plane strain was observed in room temperature grown films due to the incomplete lattice relaxation.

Scanning transmission electron microscopy (STEM) showed periodic dislocation formation at the film-substrate interface (**Figure 4**), while electron energy loss spectroscopy (EELS) provided insight into interface interdiffusion phenomena at high temperature. An atomically sharp substrate/film interface was observed at room temperature film. High-quality Raman spectra were acquired, confirming that higher nitrogen vacancy concentrations are present with the decreasing temperature of deposition. Further evidence by low-temperature flattening was observed in resistivity vs. temperature measurements, showing that the RT grown

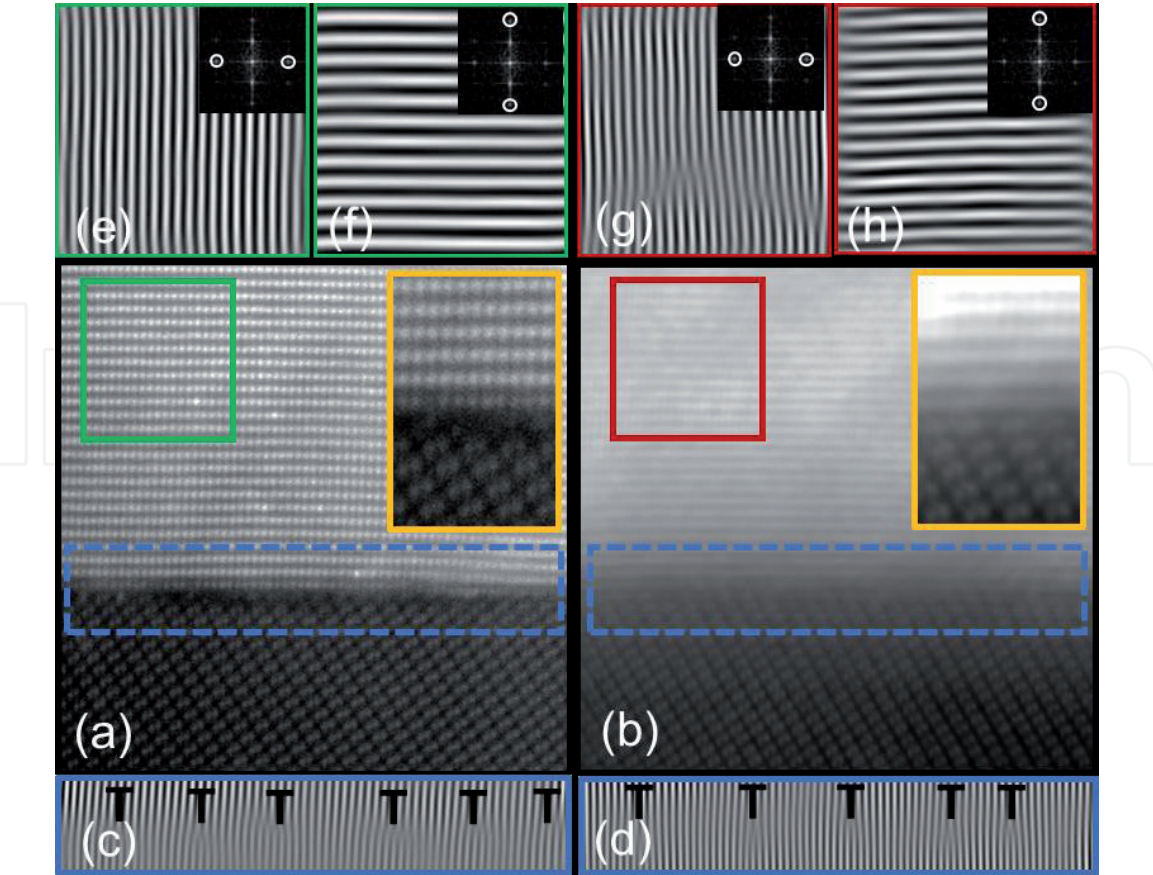


Figure 4. STEM HAADF images of TiN films grown at (a) high-temperature and (b) room-temperature conditions. The inset images show the interface between TiN and the substrate. IFFT along (110) from the TiN/ Al_2O_3 interface region (marked in (a) and (b)) in (c) HT and (d) RT growth [8].

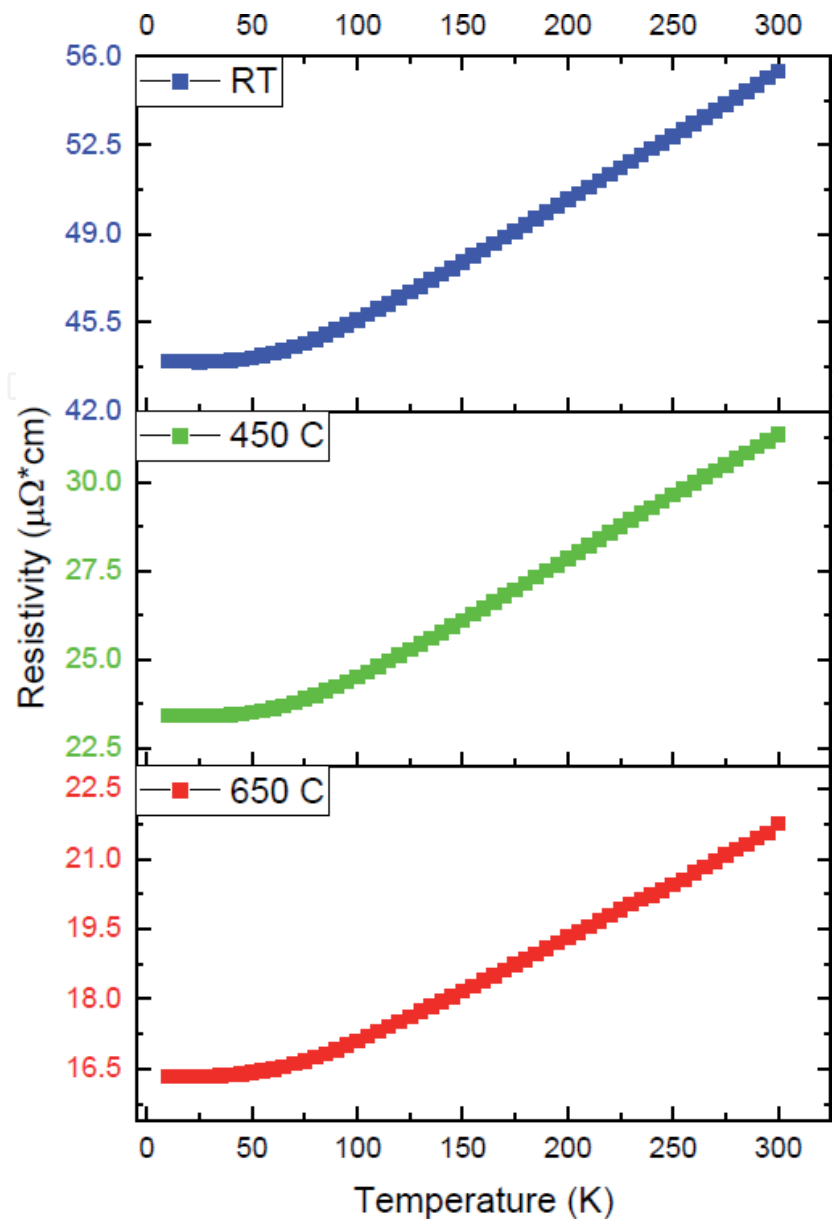


Figure 5.
The resistance vs. temperature measurements of the room-temperature, 450 and 650°C grown TiN samples. The flattening of the R vs T curves below ~35 K is due to defects becoming the dominant scattering mechanism for charge carriers [8].

film displays stronger defect scattering than HT grown films (**Figure 5**). Finally, the resistivity of room-temperature grown film was ~55 $\mu\Omega$ cm as compared to ~22 $\mu\Omega$ cm for 650°C grown films.

Resistivity of TiN films grown at different temperatures is shown in **Figure 5**. Resistivity of the titanium nitride film grown at high temperature was ~22 $\mu\Omega$ cm while room temperature sample demonstrated resistivity of ~55 $\mu\Omega$ cm, indicating comparable values and possibly opening the door for room-temperature epitaxial thin film growth for advanced microelectronic devices that require low energy budget, which will become more important with smaller gate sizes and inter-diffusion between interfaces becomes more prominent.

5. Conclusions

This chapter focused on furthering the current knowledge of thin-film epitaxy; extensive investigations were performed on the importance of deposition

temperature and post-deposition annealing while also considering the initial lattice misfit between the substrate and the film.

Post-deposition thermal processing was discussed in the case of the LSMO/MgO/Al₂O₃ heterostructures. It was observed that the behavior of thin films can be categorized into three distinct groups: (i) non-epitaxial samples (e.g. nanocrystalline and polycrystalline films, and bulk samples), (ii) epitaxial films with a small lattice misfit, and (iii) epitaxial films grown with a large lattice misfit between the substrate and the film. This work ties years of thin film annealing research together and provides the underlying theory that translates into all thin film heterostructures. Furthermore, room temperature epitaxial growth was successfully demonstrated on titanium nitride (TiN) on a sapphire substrate. This growth was rationalized by domain matching epitaxy paradigm (DME) and it was made possible at a low temperature due to highly non-equilibrium, pulsed laser deposition growth technique. The room temperature epitaxy demonstrated here transcends from TiN system and can be considered in various heterostructures. Its potential impact in the thin film industry is tremendous. Further research should be on expanding the number of material/substrate possibilities that would allow low-temperature epitaxy creates new directions in all categories of thin film science [8]. Al₂O₃ substrate was established to be the easiest substrate for its low surface reactivity. For example, silicon is highly reactive in atmosphere and will form a silicon dioxide that will not allow epitaxial growth for most materials below 500°C. However, with high-vacuum and targeted cleaning process, silicon and other industrially attractive alternatives can be considered. In the case of sapphire substrates, materials such as zinc oxide (ZnO) [36–38], bismuth ferrite (BFO) [39, 40], barium titanate (BTO) [41], and others [42–47] can be considered.

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Conflict of interest

The authors declare no conflict of interest.

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