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The impact of electron microscopy on revealing phase separation mechanisms in alloy thin films.

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The structure zone diagram and growth mechanisms of one component thin films has been worked out on the basis of electron microscopic evidences and is summarized in [1]. These mechanisms describe atomic arrangements only on the growth surface, usually recalled as kinetic segregation resulting in nucleation and growth of phases on the growth surface including their mutual overgrowth, repeated nucleation and successfully treat the effect of contaminants. A similar and comprehensive knowledge would be necessary for the films composed from two and more components. As direct observation of atomic movements is not possible we have to come to these processes by indirect methods, by deducing – aided by simulations- from all possible structural details the atomic processes leading to the formation of the structure under investigation. These structural details include the formed phases, their morphology (size and shape of grains), orientation relations (texture), surface properties as well as very local analytical information on the distribution of components and impurities. Transmission electron microscopy is one of the most direct methods for providing the above nm or even atomic scale structural information. The scope of the present investigation is to model of the growth mechanism and the basic atomic mechanisms and kinetics of self organized formation of nanostructures in two component films based on structural information provided basically by TEM. We have chosen binary systems to show on practical examples the role of TEM in revealing the phase separation processes in them. Thin films of practically non-mixing components were co-deposited. $(Ti_{1-x}Al_x)_{1-y}Y_yN$ and $Ti_{0.45}O_{0.20}N_{0.35}$ thin films were grown at 550^{o}C and 400^{o}C by reactive unbalanced magnetron sputtering in N_2+Ar and N_2+Ar+ O_2 gas mixtures, respectively [2, 3]. Structural characterization was carried out by conventional TEM using a Philips CM-20 microscope at 200 keV and high resolution measurements were carried out using a JEOL 3010 microscope at 300 keV. For chemical analysis of the films a NORAN Energy Dispersive Spectrometer attached to the CM20 microscope and a Gatan TRIDIEM Electron Energy Loss Spectrometer (EELS) on the JEOL 3010 microscope were applied.

TiN and AlN are both close packed cubic and hexagonal structures, correspondingly. They are non-mixing at the growth temperature in the whole composition range. Due to these circumstances, very special substructure can develop in TiN based alloy films. Structural characteristics typical for one phase growth (V-shaped columnar morphology and texture) have been observed also in $(Ti_{0.41}Al_{0.57})Y_{0.02}N$ thin films. The columns are composed of 3~5 nm in size fcc (TiN) and hcp (AlN) crystallites forming alternating stacks and exhibiting epitaxial relation of $\{111\}_{TiN}$ and $<110>_{TiN}//\{0002\}_{AlN}$ and $<11\text{-}20>_{AlN}$. The formation mechanism of these columns must include the growth of supersaturated solid solution of one phase hcp TiAlN, followed by a phase separation through decomposition. Only this mechanism can generate identically oriented crystallites within the columns.

Oxygen is one of the most common contaminant growing nitride films. Oxygen doping can modify both the morphology and texture of the TiN films. It has been found that beyond 15 at% oxygen doping the columnar morphology is preserved, however, the <111> texture is changed to the <001>. The detailed structure analysis of the $Ti_{0.45}O_{0.20}N_{0.35}$ oxynitride films discovered a substructure in the bulk of the TiN(O) single crystal columns. In the cross sectional TEM images it is showing up in form of fibre-like morphology and in a honeycomb-like supernetwork in the plane view TEM specimens. Electron microscopy revealed that initial phase separation by spinodal decomposition occurred in the intra-grain structure of $(Ti_{0.41}Al_{0.57})Y_{0.02}N$ films. This process, taking place still as a growth event is responsible for the formation of the epitaxial two phase nanocomposite within each column in which the similarity of the lattices of separating phases plays important role.

The observed growth morphologies for the $(Ti_{0.41}Al_{0.57})Y_{0.02}N$ films correspond to columnar morphology and the corresponding texture is developing by competitive crystal growth. In the $Ti_{0.45}O_{0.20}N_{0.35}$ films the texture changes from <111> to <100> and an intra-grain superstructure appears by a surface segregation mechanism as the oxygen content increases.

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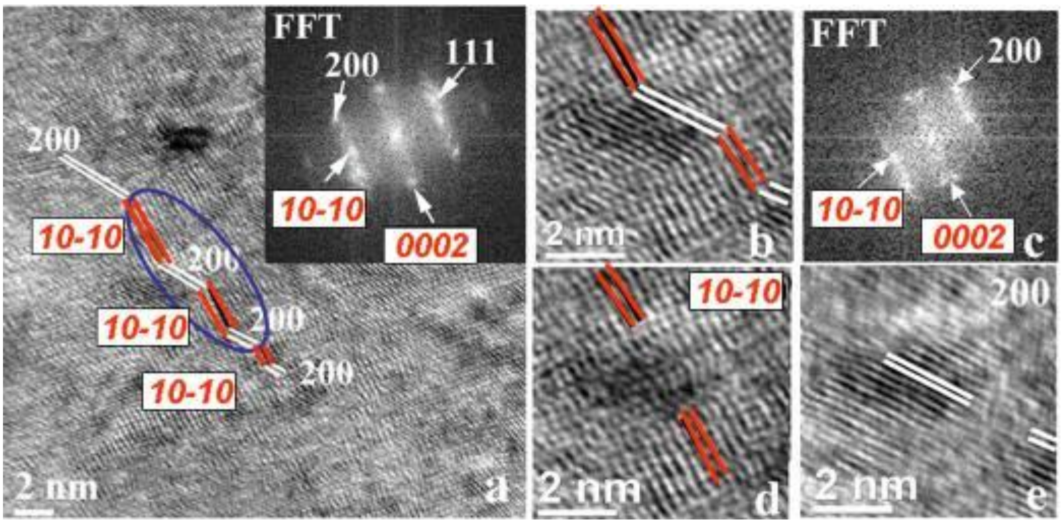

Figure 1. The HREM image of the $(Ti_{0.41}Al_{0.57})Y_{0.02}N$ film with inserted FFT pattern (a), the HREM image with two pairs of alternately stacked hcp and fcc nanocrystals (b) and corresponding FFT pattern (c); (d) and (e) are complementer HREM images taken with the hcp and fcc reflections, respectively.