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Control of Mechanical Stress as Related to Deposition Process

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Introduction

The transformation of materials from bulk solid to vapor and back to thin solid films involves processes that invariably change mechanical and optical properties. In the thin-film state, materials can exhibit characteristics very different from the bulk state; some are desirable, some are not. Advances in materials and deposition process technologies have been directed toward controlling the physical properties of condensed thin-film forms and optimizing the starting materials for a given process to perform the task at different economies of scale, sometimes at the expense of durability. While it is typical to emphasize the optical properties, the path one takes and the tradeoffs with mechanical properties, equally important are intrinsic stress, hardness, density, strength and application durability. The goal for many applications is to reproduce the bulk-like neutral physical state as closely as possible; for some applications however, it is necessary to engineer the optical and mechanical properties to achieve specific goals. An example of the latter is to deliberately replace normal incidence amorphous growth morphology with tilted, structured growth features that exhibit birefringent properties resulting from the anisotropic growth structure.

Influence of Deposition Parameters on Stress

Deposition process development has been directed toward increasing the mechanical strength, wear resistance (hardness), and the spectral, thermal and chemical stability of thin-film coatings. Specific environments and applications require different emphases. Production of the desirable coating properties is often accompanied by problematic mechanical stress that can manifest as substrate bowing, crazing and increased scatter, and catastrophic tensile cracking or film separation from the substrate. Improvements are aimed at producing thin-film coating layers with dense low intrinsic stress microstructures that ideally are amorphous [1]. Intrinsic stress is differentiated from external strain forces imposed by, for example, thermal coefficient differences between the coating and its substrate material.

Many parameters are involved in the transformation from bulk materials to thin film, each playing a role in promoting or suppressing specific film properties. The dominant parameter in achieving bulk-like film growth kinetics is the energy of deposition, a parameter determined by the deposition technique. The energy of deposition refers to the supplied kinetic energy that promotes mobility of the adatoms on the substrate surface and powers chemical reactions such as oxidation and nitriding.

The evolution from initial nucleation sites to solid film layer growth is complex in that it involves several morphological stages [2]. Isolated islands grow into clusters from which grains and columns emerge that constitute an open low-density structure. Densification proceeds with the addition of external energy, and the stresses transition from tensile to compressive.

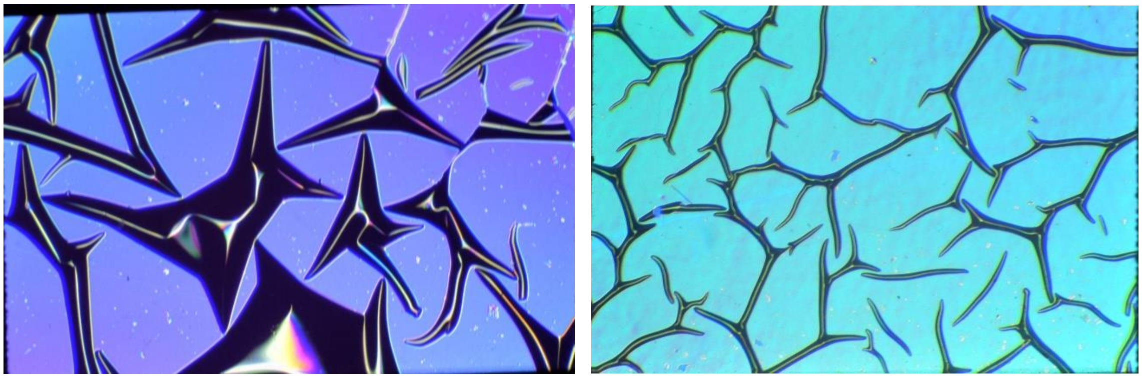

Image on the left Nomarski microphotograph of compressive stress example. Image on the right: Nomarski microphotograph of tensile stress example. Images by Samuel Pellicori.

Low-energy processes grow coarse film microstructures that are characterized by columnar features with large void volume; the result of the lower mobility energy of low-energy processes. This class of microstructure is produced by thermal evaporation from resistance or by e-beam heating with adatom energies in the range ~1-3 eV. Figure 1 is the Structure Zone Model of Dr. Anders that relates film microstructure to the energy of deposition [3]. Anders emphasizes that a multi-dimensional diagram is required to truly describe the complex growth dynamics and reactivity of thin layers. The large grains and grain boundaries associated with the porous structure of Zone 1 are the result of low energy conditions and generally possess tensile stress. The large internal surface areas and empty spaces also lend susceptibility to water vapor absorption and desorption. In these under-dense structures, the exchange of the water accompanying atmospheric humidity changes cause changes in optical and in mechanical properties, especially stress.

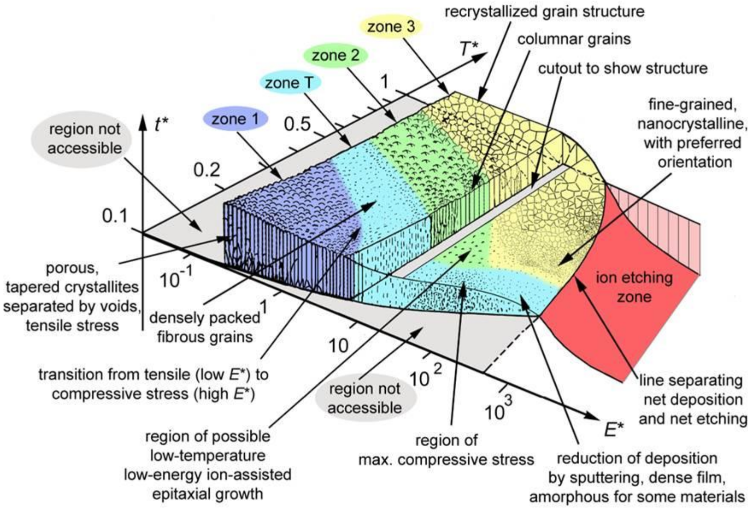

Figure 1. Structure Zone Model as modified by Dr. Anders [3].

As the energy of deposition increases with the addition of higher deposition energies and in the transition to Zones 2 and 3, grain boundary forces relax the film, resulting in a more compact microstructure. Mechanical stress and optical properties are also changed: stress transitions to compressive and the refractive index increases. In the SZM, we see the microstructure progressing from coarse and open large grains to compact smaller grain sizes as substrate temperature or energy is increased, approaching an amorphous morphology. Higher kinetic energy promotes greater mobility on the substrate surface, in turn enabling nucleation coverage that results in a denser growth morphology on the surface. High kinetic energy supplied by energetic ions substitutes for high substrate temperature in driving the layer growth to a fine-grained compact microstructure. Deposition on temperature-sensitive substrates is accomplished by eliminating reliance on in-situ bulk substrate heaters in exchange for mild ion assistance. Beyond the heat of condensation, excess energy from ion energy assistance promotes chemical reaction for oxidation, stronger bonding and adherence to the substrate. For example, while compaction increases with energy, the sputtering effect associated with higher energy density dominates over the growth rate at energies above certain values as shown in Figure 1.

Parameters affecting film morphology associated with high-energy ion-assisted processes include ion momentum and atom-to-ion ratio. Ion momentum is the product of energy and ion mass and has been shown to be the operative energy component that affects [4 -5]. The product of atom-to-ion ratio and particle momentum determines the morphology of the growing film. These parameters influence the intrinsic stress of the coating as illustrated in the Structure Zone Model in Figure 2. Typical atom-to-ion ratios are 0.2 to 0.4 for ion energies <300 eV.

High mobility energy provided by high-energy ions and plasmas is necessary to promote the growth of dense structures. A large range of energies and momenta are provided by typical deposition processes. R.F. and D.C magnetron sputtering can generate energies ~10-20 eV. High energy ion bombardment assist (IAD) was introduced to thermal vaporization processes to raise the energies to >100 eV. Ion beam sputtering (IBS) energies can exceed 100 eV to form the densest films. Energetic Ar, O, or N ions are ingredients in both processes that produce dense stable stoichiometric-composition correct coatings. Substituting heavier Xe for Ar as the plasma gas will increase the momentum of the bombarding ions. Substrate bias, incidence angle, target/gas mass ratio are also controllable parameters that affect growth morphology. Plasma-assisted deposition (PIAD) energies are >50 eV. High-energy processes, especially those involving ion bombardment, tend to produce compressive stress because of the high packing density produced. Figure 2 illustrates the behavior of stress with impacting momentum [4]. Stress reversal can be observed for energies between ~50 and 100 eV/atom.

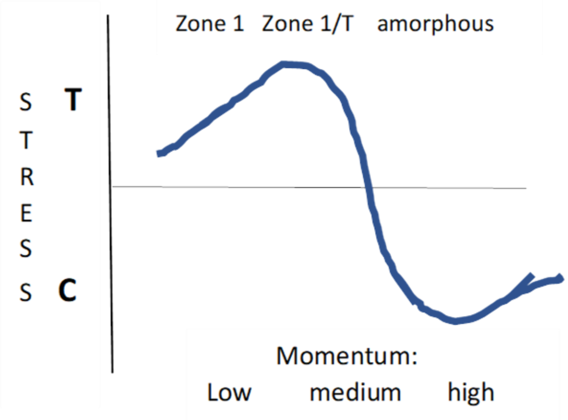

Figure 2. Relationships between stress, film microstructure, and adatom momentum in sputter deposition adapted from Ref 4.

Some general behavior is observed in relation to sputtering. Stress increases with power, decreases with pressure, and increases with thickness.

Coatings produced by high-energy magnetron and ion-beam sputtering processes exhibit nearly zero wavelength shift between ambient humid and vacuum environments, in addition to high resistance to the space radiation environment. [6]

Influence of Source Material Preparation on Film Stress

Another technique for densifying coatings is to use prepared mixed-component deposition materials in place of pure starting materials. The operating mechanism is the discouragement of the growth of large grains and columns, forcing an amorphous microstructure. This can be accomplished at lower substrate temperatures and often without the addition of energetic ion bombardment. The growth of large crystallite grains is disrupted by the inclusion of impurity atoms on the reactive surfaces. Reduction of the internal energy by deactivating the surface bonds with the foreign material reduces the internal strain, favoring a more homogeneous (pseudo-amorphous) dense growth with lower total strain. This technique consists of doping the base material compound with a few % of a chemically similar material whose atoms are larger and/or chemically reactive. As with any multi-phase constituent system, elemental impurities reduce the melting point of the system (compared to the single pure compound). They can promote more favorable compound formation with lower stress, consistent refractive index and improved mechanical properties. This technique has been used with oxide and fluoride compounds.

An exception to the “rule” that high energy processes are superior to low energy processes is encountered for UV laser coatings. High energy processes invariably cause some stochiometric unbalance in the form of fluorine loss or sub-oxide formation, both of which increase the absorption of the film. Defects at the atomic or molecular level caused by high energy impacts during deposition become centers for damage initiation.

Laser-induced damage threshold (LIDT) performance is extremely sensitive to composition, impurity and defect concentration, especially for fluoride or oxide compounds used for laser wavelengths at 355 nm and shorter. An interesting benefit is that the LIDT of these modified coatings is higher than that of pure-compound coatings, suggesting that film microstructure is more important in assuring high LIDT than the presence of chemically compatible “impurities”.

Summary

Deposition processes that employ different particle momenta to reduce intrinsic stress and improve the mechanical properties of coatings have been presented. Deposition parameters can be varied to engineer the atom-to-ion ratio and the energy of the impacting particles to control stress. Materials can be modified to simulate the influence of high-energy processes to promote amorphous film growth. The coating engineer therefore has some options for depositing mechanically stable coating layers.

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