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Inducing Grain Alignment in Metals, Compounds and Multicomponent Thin Films

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ABSTRACT

Several methods to induce grain alignment in polycrystalline thin films are discussed, in which directional effects can dominate over the normal evolution of fiber texture during thin film growth. Early experiments with ion beam assisted deposition showed the importance of channeling directions in selecting grain orientations with low sputtering yield or low ion damage energy density. Examples of this approach include the formation of biaxial fiber textures in Nb, Al and AlN. Grain orientations may also be selected by the release of stored energy during abnormal grain growth initiated by solute precipitation (Cu-Co) or phase transformation ($TiSi_2$). Other energy sources such as mechanical deformation, crystallization or compound formation may also contribute to producing desired grain alignments. In multicomponent thin films, combinations of these mechanisms provide opportunities for more specific control of grain orientations.

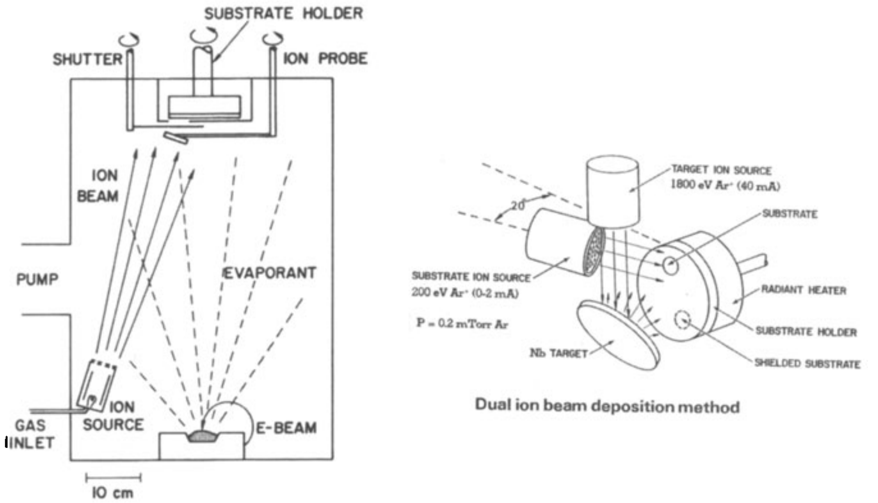
INTRODUCTION

Thin film deposition often involves bombardment of the growing film by energetic particles including the depositing atoms themselves, process gas atoms (e.g. Ar) reflected from a sputtering target, ions attracted to the substrate by a bias voltage, and ion beams directed at the growing film. The latter is usually called Ion Beam Assisted Deposition (IBAD), and gives a high level of control over the deposition environment. At the request of the organizers of the Fall 2008 MRS Symposium RR on Artificially Induced Grain Alignment in Thin Films, this paper begins by summarizing the early development of IBAD at IBM Research. Next, the effects of releasing stored energy during abnormal grain growth are discussed as an approach for selecting grain orientation. Two examples are described in which this mechanism is initiated by solute precipitation and by phase transformation.

BACKGROUND

In the mid-1970's, radio frequency diode sputtering was developing as the preferred method for depositing thin films for silicon technology and memory devices. At IBM's Thomas J. Watson Research Center, Jerome J. Cuomo was studying the effects of bias sputtering on thin film properties and recognized that an ion beam could provide a more controlled bombardment environment (ion energy, flux, angle) than the plasma in a diode sputtering system. In 1976, Cuomo and the author visited several ion source manufacturers, but none provided a configuration that could be conveniently operated within an electron beam evaporator or diode sputtering system. In 1977, Cuomo initiated collaboration with Professor Harold R. Kaufman, inventor of the broad-beam, multiaperture ion source for space applications. Kaufman designed a dished set of ion source grids which enabled the beam from a 10-cm. diameter Ion Tech source to be focused onto small sputtering targets to obtain useful deposition rates. Using that source together with a 2.5-cm. diameter Ion Tech source to bombard the growing film, a dual ion beam system was set up to simulate the effects of bias sputtering on amorphous Gd-Co magnetic alloys for potential memory applications. Ion bombardment could now be quantified and the effect of preferential sputtering on composition in these materials was measured [1]. It was also observed that magnetic anisotropy in these films displayed an azimuthal uniaxial orientation that aligned with the direction of ion bombardment. Even though these films were amorphous, local anisotropy in Gd-Co pairing gave an anisotropic magnetic susceptibility. An invention disclosure was filed in April 1979, but no publication was released.

Since the 2.5-cm. diameter ion source design was too large for flexible installations, Kaufman designed a compact 2.0-cm beam diameter ion source which was installed in an electron beam evaporator at IBM Research for IBAD experiments in the summer of 1979 in collaboration with Robert H. Hammond of Stanford University [2]. Since azimuthally anisotropic properties had already been observed in GdCo alloys, we decided to look for similar effects in Nb thin films. The limited space in the vacuum chamber resulted in the ion beam being directed at 28° from normal incidence, as shown in Figure 1(a).



(a) (b)

Figure 1. Configurations used for early IBAD studies of Nb texture in (a) electron beam evaporator [3] and (b) dual ion beam deposition system [4].

Niobium films evaporated at 1 nm/s on Si_3N_4 transmission electron microscopy (TEM) windows at 400 °C without ion bombardment showed no clear texture. Films deposited with 400 eV argon ions at 0.04 mA/cm^2 ion flux showed clear (110) perpendicular fiber texture, i.e. (110)

planes parallel to the substrate, but no azimuthal alignment. Films deposited with 800 eV argon ions at 1.1 mA/cm^2 showed clear biaxial texture with (110) planes parallel to the substrate and tilted (110) planes oriented parallel to the ion beam direction. If the ion beam had been installed closer to the (111) channeling direction at 35° from normal incidence, the biaxial texture would probably have been much stronger. No x-ray pole figure measurements were made on these films. An invention disclosure was filed in 1980 and published in 1982 with the title "Method for Controlling Crystal Orientation in Thin Films" [5].

The 2.0-cm diameter ion source was soon redesigned by Kaufman as an improved 3.0-cm diameter ion source which was the precursor of compact ion sources later manufactured by several companies including Commonwealth Scientific Corporation. More than sixty 3.0-cm ion sources were built in 1979-1981 at IBM Research and used for thin film and surface science experiments within IBM and with collaborators. A patent was issued in 1984 for the pluggable ion source design, and the 3.0-cm ion source was used for IBAD in evaporators and dual ion beam systems to explore stress modification, compound formation, tunneling layer formation and step coverage, in addition to modification of grain orientations [6]. During 1980-1982, several IBAD configurations were tested for biaxial texture in Nb, but most of the IBAD studies at IBM during that time period were focused on other properties including stress modification and compound formation, so no additional biaxial results were obtained.

In 1983, the author initiated a focused study of grain orientation in IBAD thin films by supervising an M.S. thesis project [7] by Ms. Lock See Yu, a student in the Materials Science Cooperative Studies program at the Massachusetts Institute of Technology. In this study, a dual ion beam system was configured to bombard the growing film with an Ar$^+$ ion beam at 70° from normal incidence, as shown in Figure 1(b). Without ion bombardment, strong (110) perpendicular texture was obtained at room temperature in Nb films deposited on amorphous silica substrates, as shown in the (110) pole figure in Figure 2(a). With ion bombardment, we obtained clear evidence of in-plane grain orientation (biaxial texture) in Nb thin films which grew with a strong (110) perpendicular fiber texture, as shown in Figure 2(b). The strength of the in-plane orientation was shown to increase with ion flux, as shown in Figure 2(c), although the x-ray pole figure system available could not provide quantitative information on the volume fraction of oriented grains.

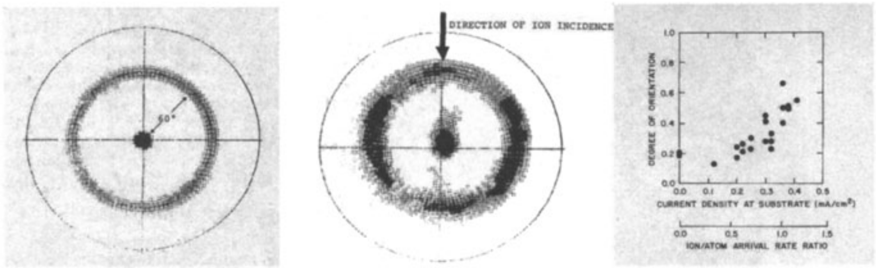


Figure 2 (a) (110) pole figure of ion beam deposited Nb film without ion bombardment, (b) with ion bombardment; (c) degree of orientation vs. ion/atom ratio [4].

The direction of grain orientation was shown to align with a planar (110) channeling direction, and its mirror image, in the BCC Nb crystal structure [4,8]. Promising results were also obtained on single crystal sapphire substrates. Ion bombardment during room temperature deposition produced a transition from a mixture of three orientations of (110) Nb parallel to (0001) Al_2O_3 to a single epitaxial orientation of (111) Nb parallel to (0001) Al_2O_3. An invention disclosure was submitted in April 1985, titled "Low Temperature Epitaxy and Polycrystalline Growth of Nb and Si on Sapphire", and published in 1987 [9].

These results led to a model for in-plane orientation based on the differences in sputtering yield (or other orienting mechanism) between channeling directions and non-channeling directions [10]. The model predicts that the asymptotic degree of orientation increases with ion/atom flux ratio, consistent with the Nb experimental results. Interestingly, the model also shows that the time (equivalently, the thickness) required to reach the asymptotic degree of alignment does not increase monotonically, but has a maximum as a function of the ion/atom arrival flux ratio. It is likely that this effect is responsible for variability of results on IBAD orientation in experiments that have not explored a wide range of ion/atom flux ratios. Biaxial texture in Al thin films was also demonstrated using IBAD by Srolovitz, Was et al. [11]. After the discovery of high-temperature superconductivity in 1986, IBAD was successfully used [12,13] to orient yttria-stabilized zirconia (YSZ) templates for the growth of high-temperature superconducting thin films with high critical current densities. The development of IBAD and other methods including inclined substrate deposition for template applications has not been pursued by the author of this paper, and is described by other authors in this Symposium. A model based on the energy density deposited in the growing film grains by ion impact was developed by Srolovitz [11] and shows that in-plane orientation may develop slowly with thickness, as in YSZ [12], or develop rapidly in the coalescence stage, as in MgO [14]. Additional factors that may cause changes in grain orientation include stress [15], deposition angle [16,17], orientation-dependent adatom mobility and shadowing [11,15,18].

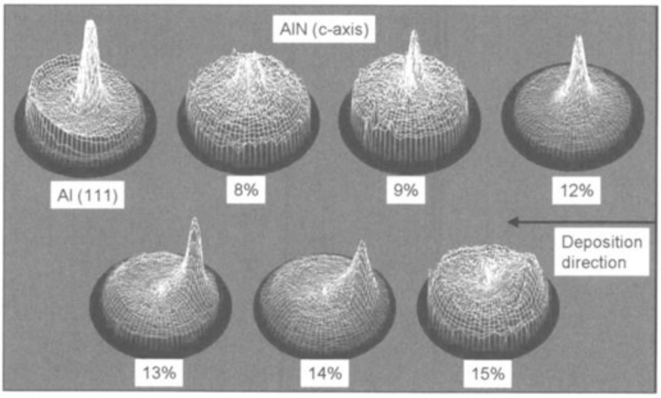


Figure 3. X-ray pole figures of Al (111) and AlN (c-axis) for $N_2/(Ar+N_2)$ gas flow ratios as indicated. The deposition direction is from the right of the figure [16].

In a study of aluminum nitride formation in dual ion beam deposition [19], the author found that AlN films grown under N_2^+ ion bombardment changed grain orientation as a function of ion energy. Also, insulating metal nitride phases such as Zr_3N_4 and Hf_3N_4 were obtained under energetic N_2^+ ion bombardment [20]. However, no detailed study of texture was made on those films. A clear demonstration of biaxial texture in AlN, measured by x-ray pole figures, was later published by Rodriguez-Navarro et al. [21] using substrate tilt to control the angle of energetic particle bombardment. Recent experiments by the author and students [16] have confirmed these observations and have shown that the AlN c-axis responds to the deposition angle (42° from normal incidence) abruptly for N_2/Ar gas flow ratios above a certain threshold, as shown in Figure 3.

These observations prompted the development of a Monte Carlo simulation model [17] that accounts for a shift in c-axis fiber texture from perpendicular to the substrate to a direction pointing towards the deposition source. In the growth of compound thin films such as AlN, the surface diffusivity of adatom species can change rapidly with a small change in reactive gas flow, changing the relative roles of lateral adatom mobility and shadowing. Additional observations on molybdenum and niobium film textures from various sputtering systems have shown the importance of deposition geometry in controlling the angles of deposition and particle bombardment, especially during the early stages of film growth that create a template for the rest of the film [18,22,23].

As film composition becomes more complex, moving from pure metals to compounds to multicomponent thin films, it is clear that more diverse mechanisms come into play in determining the eventual grain orientations in the final film. Equipment improvements have also opened up new areas for exploration. For example, R.F. ion sources without hot filaments can run on O_2 for long periods of time, allowing greater exploration of metal oxide orientations. Also, operation of magnetron deposition sources at the low end of their pressure range (1-2 mTorr) allows simultaneous operation of Kaufman ion sources at the high end of their pressure range [24]. This combination allows operation in conditions of long mean free path that maintain the directionality of both the depositing flux and the ion beam flux, which may be set at different angles to optimize orientation control. In the next section, the presence of stored energy in the film microstructure is discussed as another strong influence on grain orientations.

STORED ENERGY AND ABNORMAL GRAIN GROWTH

Thin films are metastable in many respects, and may contain stored energy which can be released to generate specific grain orientations. Here, we discuss two cases in which the release of stored energy causes strong changes in thin film texture by stimulating abnormal grain growth during annealing. While the previous discussion of IBAD effects focuses on modifying thin film properties <u>during</u> growth, annealing to change grain orientations is carried out <u>after</u> growth. The specific materials and applications will determine which approach is most feasible.

Solute precipitation

Codeposition of mutually insoluble materials may form a supersaturated solution of an alloying element within the host material. Upon annealing, the minor component may precipitate as second phase particles. At IBM Research, extensive studies of Cu alloys were carried out in the 1990's as part of developing Cu chip interconnection technology. For example, Cu and Co have very limited solubility in equilibrium. Cu alloys containing several atomic percent Co have high resistivity following deposition, since the Co atoms are dispersed in a metastable solution, as shown in Figure 4(a) [25].

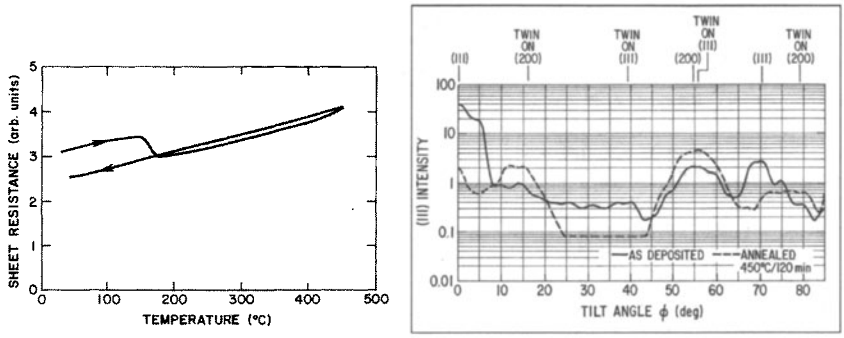


Figure 4 (a) Sheet resistance vs. temperature for Cu-Co alloy (b) (111) pole figure of Cu-Co alloy before and after annealing to 450 °C for 120 min [25]

Upon annealing to a temperature of 100-250 °C, depending on the Co content, the resistivity decreases abruptly as the Co is precipitated from solution. Simultaneously, the film stress is reduced. This precipitation process forms Co particles about 10 nm in diameter, and also causes a dramatic change in film texture. These results were found for both coevaporated and electroplated Cu-Co alloys. As shown in Figure 4(b) an as-deposited electroplated Cu-0.44 at. % Co alloy has a moderately strong (111) texture perpendicular to the substrate surface, with weaker (200) components and twin orientations. After annealing to 450 °C for 120 min, the texture is strongly (200) perpendicular to the substrate surface, resulting from abnormal grain growth of grains with this orientation. A TEM image of a large grain in an annealed electroplated Cu-0.7 at. % Co film is shown in Figure 5, with orthogonal twin boundaries typical of Cu.

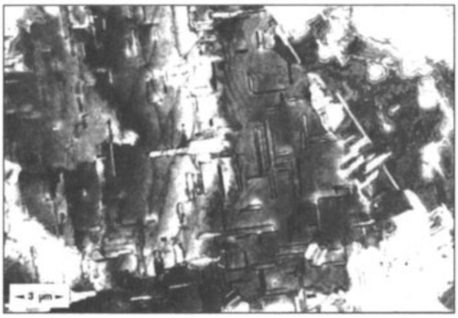


Figure 5. TEM plan view image of thinned 1 μm thick Cu-Co alloy film after annealing [25].

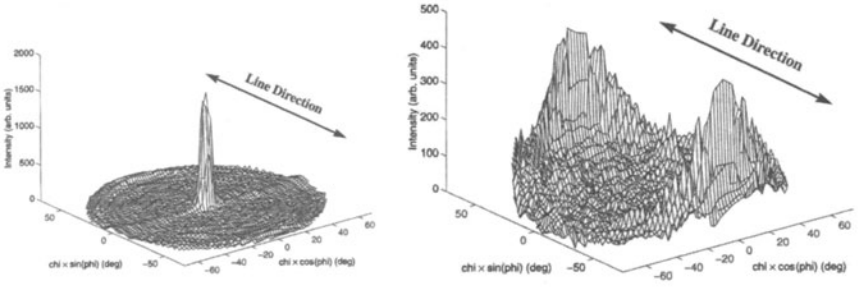
The diameter of these (200) oriented grains is in the range of 20 times the film thickness. Coupling of solute precipitation to abnormal grain growth is also called discontinuous precipitation [26], highlighting the fact that most of the precipitation of solute atoms into solute particles takes place abruptly along the moving boundary of the abnormally growing grains.

The stored energy in the Cu-Co alloys that generates highly oriented grains is released by Co solute precipitation. Both the energy of solution and the grain boundary energy density are reduced by forming Co particles at the same time as forming much larger grains. For comparison, in pure Cu, abnormal grain growth is typically observed only for annealing temperatures above 500 °C [27]. The mechanism that keeps the grain boundaries moving in Cu-Co alloys is the additional release of energy caused by solute atom precipitation. Estimates indicate that the energy density available from solute precipitation can easily exceed the grain boundary energy density [28]. In developing methods for artificial control of grain orientations, we have an opportunity to take advantage of the inherent tendency for grain reorientation provided by this internal energy source. This mechanism also draws attention to materials that might be successfully alloyed with a small fraction of second-phase material in order to introduce solute precipitation as an energy source, without compromising the desired properties of the host material.

Phase transformation

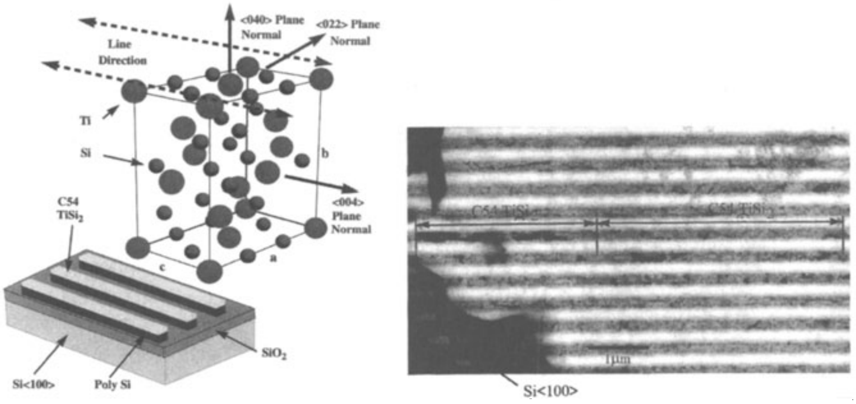
Many useful thin film materials have structural phase transformations which must be controlled to obtain desired properties. For example, the compound $TiSi_2$, used in silicon device contacts, is formed by thermal reaction of Ti with Si. The phase initially formed is the C49 structure, which has a high resistivity (50-75 μΩ-cm) and small grain size (typically tens of nm) [29]. The desired phase of $TiSi_2$ (resistivity 15-20 μΩ-cm) has the C54 structure, which is usually obtained by a high temperature anneal around 800 °C. At IBM Research, a substantial effort was made in the 1990's to extend the use of $TiSi_2$ to the smallest possible feature sizes [30] before it became necessary to use $CoSi_2$. As part of these studies, the phase transformation was examined in great detail, including its effect on grain orientations in small feature sizes. The author proposed a study of grain orientations as an M.S. thesis topic for Vjekoslav Svilan, a student in the Electrical Engineering Cooperative Studies Program at the Massachusetts Institute of Technology. His thesis, "Texture Analysis in Submicron Structures of Titanium Silicide" was completed in 1996 and the key results were published in 1997 [31]. Patterned lines of polycrystalline Si were reacted with Ti to form C49 $TiSi_2$, followed by annealing to form C54 $TiSi_2$. Narrow lines of 0.22 μm width showed a strong orientation of the C54 grains along the direction of the narrow lines. While the C49 grains were smaller than the line width, the C54 grains extended along the lines to distances about 15 times the line width. Given the small amount of material present in these patterned thin layers, the X20C beam line at the National Synchrotron Light Source was used to provide a very high x-ray flux which was able to follow the phase transformation in real time and obtain accurate pole figures. The C54 grains were found to be strongly textured with the (040) direction perpendicular to the substrate surface, and the (100) direction aligned with the narrow line direction, as shown in Figure 6. In this non-cubic structure, diffraction from the (100) planes could not be measured directly, since that scattering vector was in the plane of the sample. Instead, pole figures of the (040), (311) and (022) planes were examined to precisely determine the (100) direction as being parallel to the patterned line direction. A sketch of the orientation of C54 grains with respect to the lines is shown in Figure 7(a) and examples of long C54 grains extending along the narrow lines are given in Figure 7(b).

These results provide an example of abnormal grain growth stimulated by a structural phase transformation. The grains that grow fastest along the line direction are the grains that dominate the final population, therefore anisotropic grain growth velocity is an important parameter in selecting the grain orientation in confined structures. The resulting large grain orientation is determined by the physical constraints of the patterned film instead of an externally imposed ion bombardment direction.



(a) (b)

Figure 6 (a) (040) pole figure and (b) (022) pole figure of C54 $TiSi_2$ patterned lines [31].



(a) (b)

Figure 7 (a) Sketch of orientation of C54 $TiSi_2$ unit cell relative to patterned polycrystalline Si lines, (b) TEM plan view image of C54 grains extending along the lines, indicated by arrows [31].