From IBM (Harper) to Stanford, from IBAD-YSZ to ITaN-MgO

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ABSTRACT

This session is titled “Milestones in IBAD Texturing”. Three talks in this session contain history and status of the development of IBAD for texture, starting with James Harper, followed by Yasuhiro Iijima on the history and status of IBAD-YSZ first used for HTSC Coated Conductor. This paper continues the history including the discovery of IBAD-MgO. Subsequent developments in the understanding of the mechanisms of bi-axial texture through experiments and theory are reviewed to arrive at the present but not complete understanding. New in-situ characterization needs are discussed and new tools to affect the texture development are suggested.

INTRODUCTION

The title of this session is “Milestones in IBAD Texturing”. The first talk and paper is Jim Harper’s review and history of the early results on “Inducing Grain Alignment in Metals, Compounds and Multicomponent Thin Films”, including up to his recent results[1]. It was due to his (and others at IBM-Yorktown) efforts that Harold Kaufman developed the compact ion beam source that has made ion texturing possible. This came to fruition in 1979, in time for the summer visit of the author to learn about ion beams and their effect on thin films.

The second talk and paper covers the important development of IBAD-YSZ for the High Temperature Superconductors application known as Coated Conductors. This was originated by Dr. Iijima at Fujikura Ltd., in the early 1990’s[2]. The success of this development showed that this could be a route to the successful answer to the demanding requirements of the ceramic materials requiring essentially kilometers of biaxial texturing on top of flexible metal tapes.

The third talk and this paper are in part the description of the discovery and development of a more economical method, IBAD – MgO, using ion texturing at nucleation, or ITaN[3]. The idea for this originated while at IBM the summer of 1979, while discussing observations of texturing during certain sputtering operations with Harper. The vision was to affect the nucleation of atoms as they nucleated using ions, and to observe the effect with RHEED (Reflection High Energy Electron Diffraction) in real time. It is this in-situ characterization that distinguishes this development. Biaxial texturing was being observed after sputtering and ion beam IBAD, but there was no idea of when this was occurring, and usually found only in thick films approaching a micron in thickness. That mechanism is by evolution, as described by Bradley et al in 1986[4].

The current research results at Stanford are in the papers by James Groves.[5, 6]
Early Efforts at Stanford

Motivated by the success with YBCO on IBAD-YSZ by Iijima[7], Paul Arendt (LANL)[8, 9] and Reade and Berdahl (LBL)[10], an effort was initiated at Stanford University under the sponsorship of Ted Geballe and funded by Paul Gant at EPRI and made possible by the new Molecular Beam Synthesis (MBS) facility (funded by a proposal of Mac Beasley) that was designed with the ITaN requirements in mind: a RHEED system, Kaufman ion source, evaporation sources, rate control, and 4-axis sample orientation. Graduate student Khiem Do initiated the work using MgO because it has a (100) preferred growth and thus did not require overcoming another texture (as is the case with YSZ), and because its lattice constant is not too bad for YBCO.

The procedure used involved fixing the ion flux and increasing the MgO flux in steps, pausing 20 seconds before increasing it again, watching the RHEED for a pattern different from the amorphous pattern of the SiN bed layer. A RHEED pattern did appear at a certain flux, on the very first attempt. The ratio of ion to MgO flux at this point is called the critical ratio. For later reference note that until the critical ratio is reached in this mode there is no deposition of MgO—it is all sputtered off by the ion beam. This we call the Stanford mode. It was found that the RHEED pattern improved as the deposition continued at the same ratio, until saturation was reached. This occurred at a thickness of between 60 and 100 Å. In order to measure the texture quantitatively by XRD, a thick MgO layer was deposited homoepitaxially at some higher temperature, say 400 °C. Connie Wang continued this research, exploring many factors to find the best conditions[11, 12]. The factors that were found to be important included: temperature, ion/molecule ratio, angle of ion beam, and energy of ions. TEM images taken at various stages during the process seem to show that during the period following the initial stage the MgO formed cube shaped islands that did not touch until approaching compete coverage, and the orientation of each island is far from in-plane, perhaps 15º away. As they coalesce approaching complete coverage the angle is reduced greatly. This has been ascribed to grain-boundary energy minimization.

Further research at Stanford was not possible for a period (from 1998 till 2003). At Caltech Brewer and Atwater[13] in 2002 published their research using improved techniques in the art and science of RHEED together with TEM. This work differed from the Stanford mode by starting with a lower ion flux, somewhat less than the critical value. Thus the MgO deposited with little ion sputtering, with full coverage as an amorphous or micro-crystalline film. Suddenly at a thickness of about 20-30 Å the RHEED changed to a textured pattern.

**THEORY: MOLECULAR DYNAMICS SIMULATION**

At the same time period, Zepeda-Ruiz and Srolovitz (ZS) used atomistic simulations[14] to determine how an ion beam can control the crystallographic texture of a film by modifying the island nucleation process. They used the special case of MgO and 600 eV Ar⁺ ion beams, and the substrate bed of amorphous SiN (Si₃N₄). As an illustration of the effect they compared two island sizes: one is 3x3x3 unit cell (about 1.3x1.3x1.3 nm for MgO), the other is 5x5x5 unit cell (2.1x2.1x2.1 nm for MgO). The result of a single Ar ion impinging along the channeling direction parallel to the (011) axis is dramatic: In the first case the island is completely amorphized, with some sputtering away of atoms, while the larger cell suffers very little damage and sputtering. Simulations for different angles of incident ion showed that the magic channeling
direction is only effective for island sizes starting at about 2-3 nm, the differential with angle increasing as the size increased. A sobering finding is that the total sputtering yield minimum width is broad, about ±15 degrees (for the relatively low energies used in IBAD). This ultimately places a limitation on the expectations for biaxial alignment from this process alone. They extended the simulations to include many ion impacts at variable angles, still for the special cases of 3x3x3, 5x5x5, and an infinite atom cube. To arrive at a description for all sizes of nuclei they apply an exponential fitting function to these three data points, arriving at the curves in Figure 1. The parameters are the size of the nuclei (film thickness as an approximation) and the ion / molecular flux ratio, ρ. These curves are for the case of Ar ions along the MgO (or any rocksalt-structure material) (011) channeling direction. They also show an example of the difference when the angle to the channeling direction is varied, with the result showing the dependence of the critical island size on island orientation with respect to the ion beam, i.e., where dL/dt =0. This figure is useful for discussing and describing the results of several of the well characterized published experiments, leading to some understanding and limitations of the basic understanding of the mechanism.

There are several issues to note about this simulation: This figure does not include the capillarity effect at small island size, which leads to the concept of a critical nuclei size even without the sputtering effect of the ions. This is evident in Figure 1 at the low ion flux and small island size. Another issue is: do the simulations mean actual sputtering of the atoms away from the growth region? The answer is yes, and this is defined where the atoms are moved 6 Å away from the surface. There is certainly damage (amortization) as well until grains crystallize when the conditions are right---in the region in Figure 1 above zero growth and until the size reaches about 3 nm.

One thing to note immediately is that the growth rate is zero for a ρ of about 0.55 (extrapolating where the curve passes through the origin). This is called the critical ρc, where there is no net deposition. This agrees well with the results of Caltech (Brewer-Atwater[13], Brewer thesis), and the Stanford results of Wang[11, 12]. However this does not agree with the
results of Findikoglu-Matias[15, 16] (LANL), who find a value of greater than 1. We assume that there is a difference in the method of the determination of the fluxes. Caltech finds the best inplane alignment at a \( \rho \) of 0.43, thus as the shutter is opened there is a positive net island growth. If Figure 1 is followed the growth rate should follow the curve for the value of the \( \rho \) at the start and thus the rate of growth increases in time as the nuclei size increases, and thus the channeling differential increases. (We note here that we now measure the accumulation vs. time via a microbalance system---this will determine the time evolution of mass deposited, and check this assumption of the theory.)

Caltech used in-situ RHEED analysis and ex-situ TEM electron diffraction on the same SiN windows to monitor the development in real time as the thickness increases. They found that initially the deposit is amorphous/disordered fiber textured till a certain thickness of about 3 nm is reached, where suddenly the nuclei of biaxial textured MgO appear. The in-plane texture improves up to the thickness where the diffraction intensity is a maximum, and most of the film has transformed from amorphous to crystalline. They ascribe the texturing to the mechanism discussed above of ion beam minimal damage along the (011) direction and damage to the other orientations, resulting in orientated seeds in the disordered matrix. These seeds lead to a transformation of the surrounding region by a solid phase crystallization process, and is called in general due to “anisotropic ion damage”.

A different approach was taken earlier at Stanford, where the value of \( \rho \) was experimentally determined by increasing the MgO flux in steps while holding the ion flux constant. The RHEED was monitored at each step-increase in MgO flux for a period of 20 sec (at an average MgO flux of 0.1 nm/sec) before increasing the MgO flux and thus decreasing \( \rho \). The value where the RHEED displayed the first pattern was taken as the \( \rho_c \). (As will be discussed later a new experimental technique, the microbalance, will examine the issue of is there actually deposition before this.) The LANL technique is similar. However the Stanford and the LANL experiments do not seem to show the delay in the crystallization till after a period of amorphous film growth, as seen in the Caltech process. Rather it seems that the amorphous/disordered fiber textured phase is not seen before the appearance of the RHEED pattern. However Caltech used a more sensitive RHEED method, including subtraction of the substrate diffuse pattern (this is now being repeated at Stanford with similar sensitivity). Assuming there is no disordered growth, using Figure 1 as a guide, this process would proceed along the curve at the \( \rho_c \) or slightly above (smaller \( \rho \)) till the size/thickness of 2-3 nm is reached and the channeling selectivity is in play. Note in this case the nuclei are separated from one-another; the starting point is a bare substrate. The higher ion beam flux used in the Stanford and LANL experiments have been argued to give rise to another mechanism, namely “anisotropic ion sputtering”, rather than the Caltech “anisotropic ion damage”. In both the Stanford and LANL experiments the smallest \( \Delta \phi \) in-plane was found very close to \( \rho_c \), supporting that proposal. Another supporting fact is that the value of the best in-plane \( \Delta \phi \) is about 3° for the LANL, 6-7° for Stanford, and 10° for the Caltech. The reason for the larger value for the “anisotropic ion damage” process maybe that the seed nuclei have the range of alignment given by the ion channeling process, and as simulated by ZS, this has a range of \( \pm 15 \) degrees. As the seed grows using the neighboring amorphous material each seed-crystal is locked in place. However, in the Stanford work, where the starting condition is the bare substrate, TEM images taken at various stages in the growth seemed to show individual small crystallites separate from another and with this span of orientation, \( \pm 15 \) degrees. However the final orientation at complete coverage has narrowed to 6-7°(and 3-4° for LANL). How this happens is still unknown, but a process of grain boundary energy minimization has been
proposed. This may be possible if there is separation between the grains until the final completion of coverage is attained. This is aided if the grains are mobile, i.e., not strongly bonded to the bed-substrate.

We note that there is uncertainty as to when the improvement occurs. There is even speculation that this may occur during the heating up and/or during the homo-epi process. We propose to examine this carefully using the in-situ RHEED as well using ex-situ TEM, XRD (including synchrotron GIXRD), and AFM.

Sometime in the period 1998 the knowledge and techniques developed at Stanford were transferred to LANL by visits of staff member James (Randy) Groves, sharing unpublished data and Wang’s thesis, and ongoing discussions. Groves and Paul Arendt [17] did extensive development of the MgO-IBAD as well as the “stack” of the other thin films that make up the package that makes for a successful Coated Conductor. This technology was then transferred to SuperPower, who have successively incorporated this technology with their MOCVD process of growing YBCO. SuperPower[18, 19] is now producing Coated Conductor at 360 m/hour. IBAD-MgO is now in production for Coated Conductor in Japan (Iijima[2] and Yamada[20]), and in Korea (S-I Yoo[21]).

NEW EFFORT AT STANFORD

Later a new effort was introduced at Stanford thanks to a grant from the Korean Electrotechnology Research Institute (KERI) in 2003. This made possible the design and construction of a new dedicated “Research on the Mechanisms of Ion Beam Assisted Deposition” facility. With the help of visiting students Wouter Baake of Twente University, The Netherlands, and Sung-Ho Hong of Seoul National University, Korea, this facility has been installed and is being used by a Materials Science student of Prof. Bruce Clemens, James (Randy) Groves.

In the planning for this new effort it was realized that two models for the MgO-texturing have evolved: The Caltech mode where there is no delay in the formation of the MgO film after the shutter is opened and the percentage of material sputtered away is small, and the Stanford mode, where most of the film is sputtered away, operating close to the critical ratio. Thus it seems important to monitor the mass accumulation in real time, while simultaneously monitoring the RHEED pattern at the same point of the film. A quartz crystal microbalance was designed and installed. Because the ion beam can deliver 100 mW/cm² of energy, good thermal heat transfer and bonding is important. For good ITaN growth and RHEED monitoring a smooth surface is required. The initial results are given in Groves’ paper[5,6]. It is clear that the microbalance is giving us new and surprising results to consider.

Future Needs for In-situ Characterization of Morphology and Chemistry

Having these two in-situ characterization tools (RHEED and Microbalance) makes it clear that other characterization of morphology and chemistry are needed in order to make progress in our understanding and the control of the mechanisms of the IBAD-ITaN process. The in-situ tools are in addition to the ex-situ characterization being done:

- Ex-situ snap-shots during interrupted process:
  - TEM.
  - AFM.
These ex-situ tools are important, but it is now clear that in-situ tools are very valuable. Some of the possible ones are:

- **In-situ in real time:**
  - EELS-RHEED (differacting species identification).
  - Bi-axial texture analysis by RHEED (snap-shot if rotate substrate, or in real time if incorporate beam deflection).
  - Mass Spectrometer (Sputtered species).
  - SEM (Installed in-situ).
  - AFM (Installed in-situ but requires interruption for moving substrate).
  - TOF-ISARS: Monitor composition of surface-when is coverage complete?
  - LEEM.

EELES-RHEED appears very important----the chemical atomic species from the material doing the electron diffraction would be identified. In addition, the pass-energy feature would remove the RHEED electron scattering from the background and pass only the elastically diffracted electrons. This would greatly clarify the onset of different structures during the IBAD-ItaN process.

The Bi-axial texture analysis software is installed. At present it requires stopping the IBAD-ITaN process at stages and rotating the substrate by 10° while RHEED data is taken and analyzed. We do not know if this interruption is a perturbation to the growth process. An alternative that permits no interruption is to periodically deflect the angle of the beam by the same angle.

It is important that both of the latter two RHEED modifications are available commercially from Staib, the maker of our RHEED.

A mass spectrometer would have to be installed inside the chamber, without the normal flange. However this appears do-able. As we extend our research to elements in the bed-substrate and in the ITaN material the mass range of the spectrometer would have to cover these elements. Installing a SEM is feasible but challenging, but the benefit of observing the morphology in real time would be very important. The lower cost of a donated used system could make this possible. Installing an AFM inside the chamber (not totally in-situ) would be a challenge, including the mechanism for transferring the substrate to the AFM location.

TOF-ISARS would be easy to install and could be an important in monitoring the chemistry of the top surface. However it is very costly.

LEEM or in-situ TEM would be extremely interesting. The cost and physical requirements make this very difficult.

**New Tools for Effecting Texture Development:**

- Temperature, both during the initial stage and in the later stages. The earlier Stanford work found 300 °C not as good as at room temperature. This needs to be examined at all stages, for example in the later stage of coalescence as the grains align.
- Energy applied locally at the atomic level:
  - Low energy ions, down to 15 volts is available.
Photon assist during IBAD: The Rauschenbach group at the University of Augsburg in 1996–7 showed an effect of a Hg arc lamp, (with 500 mW/cm² at the substrate) on the TiN IBAD texture[22].

- There has been the suggestion of laser excitation of atomic levels to enhance the motion of atoms to lower energy positions.
- Electron beam heating, including that of the RHEED beam, has been shown to effect the crystallization of amorphous material[23].

**Growth beyond the initial stage:**

The effort is now focused on the initial stage of alignment. What about the development as complete coverage is approached?

- Caltech mode is assumed to have complete coverage from the beginning. When the thickness is ripe for the ion damage induced crystallization the seed is not free to move to minimize grain-boundary energy (locked in by complete coverage).
- Stanford mode is assumed to have isolated nuclei that survive and grow as separated islands. TEM shows them with large angles (± 15°). These are free to move on the bed till they connect and then grain-boundary energy minimization results in orientation to ∆φ of 6-7° (3-4° for LANL).

The above models should have a dependence on the bond or interface energy between the MgO (in that case) and the “bed” material; say the SiN or a-Y2O3, etc., particularly in the Stanford case. Therefore the interface energy needs to be quantified, and tested by choosing different amorphous bed materials, such as SiN, Y2O3, Al2O3, SiOx, and a-metals (the conductivity could be a factor) and a-TiN, etc. Also the degree of ion etching on the bed could be a factor.

If we are right that the islands are free to move during the time before coalescence the prospect that the orientation might be influenced by an external force could be examined. One example might be an electric field acting on a certain IBAD material that is polar.

**SUMMARY**

- Increased understanding will come from in-situ characterization.
- Have only barely touched the possibilities:
  - Parameters include: ion/atom ratio, bed material and condition, temperature, ion energy, ion species.
  - New materials for the ITaN: oxides, nitrides, metals, etc.
  - New tools: photons, electrons, and multiple ion beams.
- Goals:
  - Understanding of the basic mechanisms of IBAD-ITaN.
  - Better alignment—what is the limit? Will application to semi-conductors, solar-cells be a possibility?
  - Faster and cheaper: Applications that depend on low cost processing (as is the case for Superconducting Coated Conductors, later for solar-cells)
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