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ABSTRACT

The type and partial pressure of oxidant mixed with argon can affect the selective resputtering of Bi in composite-target, magnetron-sputtered Bi-Sr-Ca-Cu-O films. Comparative studies using oxygen and ozone show that ozone is a more potent oxidant, as well as a more potent source of resputterers, than is oxygen. Severe resputtering from ozone is significantly reduced by a -40 V potential on the sample block. We suggest that oxygen causes resputtering by forming O_2^+ , which interacts with the target to produce energetic O^- . In contrast, ozone may form lower-energy O^- by electron impact in the dark space. Negative oxygen ions from the target itself may be responsible for a background resputtering effect. Our results and those found for Y-Ba-Cu-O by others are comparable. Bi in Bi-Sr-Ca-Cu-O behaves as Ba in Y-Ba-Cu-O, with regard to selective resputtering; furthermore, the response of Sr, Ca, and Cu to oxygen in sputtered Bi-Sr-Ca-Cu-O is similar to what is observed for Cu in Y-Ba-Cu-O.

INTRODUCTION

Compositional control of magnetron-sputtered Bi-Sr-Ca-Cu-O films from composite-targets can be hampered by bismuth loss and its dependence on a variety of processing parameters.^{1,2,3} The dependence of cation deposition rate on substrate position, shown in Fig. 1, illustrates that resputtering effects are significant, particularly for bismuth. As bismuth appears to be most susceptible to resputtering, the effect is considered to be selective. Because the selective resputtering of bismuth is exacerbated by heating the substrate, *in situ* thermally processed films are more susceptible to bismuth loss than films deposited at lower temperatures. For on-axis sputtering geometries the resputtering problem presents a substantial barrier to developing or even understanding *in situ* thermal processing of sputtered Bi-Sr-Ca-Cu-O.

The magnetron environment is rich with potential resputtering species. These resputterers can be placed into two categories. First, there are negative ion resputterers that may form near the target and subsequently accelerate toward the substrate. Second, there are resputterers formed by neutralization collisions between the sputtering ions and target atoms. Resputterers of the first kind gain their energy from acceleration in the electric field near the target; the second kind gain their energy kinematically from collisions with the target.

The first type of resputterer can occur when target atoms are sputtered as negative ions.⁴ (In the case of the cuprate high- T_c materials, oxygen atoms in the target are likely to sputter as negative ions.⁵) Furthermore, it is possible to generate negative ions from an oxidant added to the sputtering gas. The negative ions may neutralize before they reach the sample, after gaining significant energy from the electric field near the target.⁵

A common example of the second type of resputterer occurs when argon ions suffer neutralization collisions with massive target atoms. For atoms as massive as bismuth, the reflected argon neutrals may have sufficient energies to cause resputtering. The distribution of these neutral resputterers, however is much less directed toward the substrate than that of the negative ions accelerated away from the target.

Although direct determination of resputtering species and their energy distributions is quite difficult, there are resputtering effects that can be linked to processing parameters for film deposition. By compositional analysis of Bi-Sr-Ca-Cu-O films deposited onto heated substrates the effects of a variety of parameters can be compared. We shall focus on the role of the oxidant -- its type and its partial pressure -- in determining the severity of the selective resputtering of bismuth.

EXPERIMENTAL DETAILS

Films were prepared by on-axis dc magnetron sputter deposition from 2-inch diameter targets of Bi-Sr-Ca-Cu-O material. A schematic of the apparatus is shown in Fig. 2. MgO single-crystal substrates were bonded to a heater block, which was positioned so that the sample-target spacing was roughly 2 inches. A dc power supply allowed the potential of the heater block to be adjusted relative to ground by ± 40 V. Gases for sputtering were bled into the chamber through metering valves, and their mixture was adjusted by use of a capacitance manometer and a residual gas analyzer. Typical magnetron conditions were -200 V at 0.1 A. In 90 minutes, roughly $300 \mu\text{g}/\text{cm}^2$ ($\sim 0.3 \mu$ thick) of $\text{Bi}_4\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ could be collected on an "ambient" substrate. These ambient

substrates were heated to roughly 100 °C by the magnetron in 20 mTorr of argon.

In order to study the oxidant-related effects, films were deposited on substrates heated to roughly 700 °C. Oxygen or ozone was mixed with the argon sputtering gas. For each oxidant, a series of films was made at different oxidant partial pressures, keeping the total sputtering pressure fixed at 20 mTorr. Films sputtered with oxygen were deposited from a $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ target; films sputtered with ozone were made from a $\text{Bi}_4\text{Sr}_2\text{Ca}_{2.4}\text{Cu}_3\text{O}_x$ target.

Compositional analysis of the films was done by x-ray fluorescence spectroscopy, standardized against a sample that was further analyzed by inductively coupled plasma - atomic emission spectroscopy techniques. The fluorescence technique was used to determine the mass density (in $\mu\text{g}/\text{cm}^2$) of each element in a given film, thereby enabling a comparison of net deposition rates among the Bi-Sr-Ca-Cu-O cations. By normalizing the mass densities of each element to those in ambient films made from the same target, results from targets of different compositions could be compared.

RESULTS

As can be seen from Figs. 3 and 4, addition of either oxygen or ozone to the sputtering gas has an effect on the bismuth content of the film. For low partial pressures of oxidant, there is an enhancement of bismuth content, relative to the case of no oxidant. Higher concentrations of either oxidant, however, cause substantial bismuth loss and noticeable loss of the other cations. The results

presented for strontium in Figs. 3 and 4 are representative of the behavior of calcium and copper as well.

The substantial bismuth loss caused by ozone can be largely reduced by applying a -40 V potential to the sample block. In contrast, there is no significant bias effect observed for oxygen. The bias effect with ozone is illustrated in Fig. 5.

DISCUSSION

The data in Figs. 3 and 4 show that oxidants in the sputtering gas can have a substantial effect on the degree of resputtering. The effect of oxygen partial pressure on magnetron-sputtered Bi-Sr-Ca-Cu-O films is similar to what is observed in studies⁵ on magnetron-sputtered Y-Ba-Cu-O in oxygen-argon mixtures. Bismuth in Bi-Sr-Ca-Cu-O, like barium in Y-Ba-Cu-O, is selectively resputtered. Furthermore, the effect of oxygen partial pressure on strontium, calcium, and copper in Bi-Sr-Ca-Cu-O is similar to that on copper in Y-Ba-Cu-O. Simply stated, as oxidant partial pressure is increased, the oxidant exacerbates preferential resputtering of one element and eventually causes resputtering of the other elements as well.

In the limit of no oxidant, the resputtering is likely caused by negative oxygen ions sputtered from the target. This background resputtering effect can be somewhat reduced by small partial pressures of oxidant in the sputtering gas. The role of the oxidant may be largely chemical, for these low concentrations. Oxides and other reacted forms of the metals in the film should be less susceptible to resputtering effects than the pure metals. As indicated in Figs. 3 and 4,

considerably less ozone than oxygen is required to stabilize the film against resputtering. Considering the relative reactivities of ozone and oxygen the difference in amounts required to achieve similar effects is understandable.

As the oxidant partial pressure increases, the effect of the oxidant becomes more complicated. In addition to enhanced oxidation of the depositing film, there is a severe resputtering effect. By considering the effect of either oxidant alone it is difficult to establish the exact resputtering mechanism, other than to suspect that the resputterers are negative oxygen ions. By comparing the effects of ozone and oxygen, however, some additional insight is gained.

From Figs. 3 and 4, the qualitative similarities of the effects of ozone and oxygen are apparent. It is also clear that ozone is more potent than oxygen; the effects exhibited by ozone in the 0 - 1 mTorr range of partial pressures are observed for oxygen in the range 0 - 10 mTorr.

A significant difference between ozone and oxygen is evident from Fig. 5. Whereas there is no significant bias effect with oxygen, a -40 V bias has a substantial effect on film composition when ozone is used as the oxidant. Evidently, some unneutralized negative ions reach the substrate when ozone is present. As for oxygen, we must conclude that the negative ions arrive at the substrate with significantly greater energies and/or that they arrive as neutral particles.

The difference in bias effect for oxygen and ozone may depend on the regions of the magnetron where these oxidants produce the negative ions, as well as the mechanisms by which the ions are formed. From the schematic of potential as a function of position in the magnetron (Fig. 2) the importance of the location of negative ion formation can be inferred. If oxygen were to produce

negative ions at the target surface, while ozone were to form negative ions in the dark space away from the target, the difference in bias effect would be understandable. Furthermore, such a situation might suggest that the mechanisms of ion formation are different for oxygen and ozone in the magnetron environment.

We now focus on the possibly different mechanisms of ion formation for ozone and oxygen in the magnetron. First, we consider oxygen. For the oxygen partial pressures required to cause a severe resputtering effect, there must be significant amounts of positive molecular oxygen ions. We must therefore consider the consequences of a positive oxygen ion flux at the target.

In the most general terms, the positive molecular oxygen ions may interact with the target to produce negative oxygen ions at the target surface. The specifics of the process might be a collision (involving the incident positive oxygen, a target atom, and secondary electrons) resulting in negative oxygen ion production at the target surface. Another possibility is that the incident oxygen ion reacts with target atoms; the consequent bonded oxygen atoms would eventually be sputtered from the target as negative ions. In either case, the result is negative oxygen ions leaving the target with potential energy from the high negative voltage of the target.

In contrast to oxygen, ozone has significant resputtering effects at much smaller partial pressures and generates negative ions that are stoppable by a -40 V bias. The high dissociability of ozone may facilitate the production of negative ions by electron impact in the dark space. Low-energy electrons should be more effective in such a process.^{3,6} In the discharge, such low-energy electrons are in abundance in the dark space away from the target. Hence, it is

plausible that ozone dissociation by electron impact creates negative ions with significantly lower potential energies than those generated at the target surface. These lower-energy negative ions could be stopped by a -40 V bias applied to the sample block, provided that they retain their charge upon traversing the plasma.

Whereas oxygen ions formed at the target surface are unlikely to be affected by a small sample bias whether or not they neutralize, ions formed (in the dark space) at potentials closer to that of the sample must retain their charge in order to exhibit a bias effect. Either both types of resputterer maintain their negative charge, or there is some mechanism by which high energy ions are more likely to neutralize than low-energy ions. The latter suggestion implies a link between neutralization and ion energy. Such a link is indeed possible. In order for a negative oxygen ion to neutralize by collision with an argon atom, for example, it must have an energy of roughly 15 eV or greater.⁷ (For heated substrates it may not take much energy for a resputtering event to occur, particularly for the apparently volatile bismuth atoms.) If oxygen and ozone differ with respect to the energies with which they form negative ions, it is possible for neutralization to occur in one case and not the other.

The discussion above suggests that the observed dependences of resputtering effects on type and amount of oxidant can be understood as follows. Oxygen and ozone both have a stabilizing effect against a background resputtering at low partial pressures. This background resputtering is likely a result of target oxygen sputtered as negative ions. As oxidant partial pressure increases, the chemical benefit of the oxidant is overcome by oxidant-induced resputtering effects. In the case of oxygen, positive molecular oxygen ions may interact with the target to produce negative ions having the target potential; these ions may not be affected by a -40 V bias because of their high energies, as well

as their ability to neutralize. Ozone, in contrast, may form negative ions by electron impact in the dark space, creating less energetic ions, some of which arrive at the substrate unneutralized and with low enough energy to be stopped by a -40 V bias.

Although the scenario presented above accounts for the observed effects, it is difficult to verify by direct measurements. Some estimates³ of the relative densities of various species in the magnetron environment, as well as the relative effects of electron impact on oxygen and ozone in the magnetron environment suggest that the scenario is plausible.

CONCLUSION

Studies of Bi-Sr-Ca-Cu-O films sputtered on-axis from composite targets in a planar magnetron show that oxidants mixed with the sputtering gas can effect the degree of selective resputtering of bismuth. In small amounts, oxygen and ozone reduce the resputtering effect. For higher partial pressures, however, the oxidants cause severe resputtering. The effect of oxygen partial pressure on magnetron-sputtered Bi-Sr-Ca-Cu-O films is similar to what is observed by others for magnetron-sputtered Y-Ba-Cu-O in oxygen-argon mixtures: as partial pressure increases, the oxidant exacerbates preferential resputtering of one element and eventually causes resputtering of the other elements as well.

Whereas oxygen causes severe resputtering when it is a significant fraction of the 20 mTorr of sputtering gas, ozone causes comparable effects at much lower partial pressures. Furthermore, the resputtering effects from ozone are

substantially reduced by a -40 V bias on the sample block. The sample bias has no substantial effect for oxygen.

The experimental results may be accounted for by a background resputtering effect from oxygen in the target and an oxidant-induced resputtering effect from the added oxygen and ozone. Oxygen may bring about resputtering by forming positive molecular oxygen ions, which interact with the target to produce high-energy negative oxygen ions at the target surface. In contrast, ozone may form lower-energy negative ions by electron impact in the dark space. These lower-energy ions can reach the substrate unneutralized and can be stopped with a -40 V bias on the sample block.

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REFERENCES

1. R.T. Kampwirth, P.H. Andersen, D.B. McDonald, D.J. Miller, K.E. Gray, Z.F. Sungaila, B. Balachandran, and A. Wagner, *Appl. Phys. Lett.* **55** (20), 2135 (1989).
2. R.T. Kampwirth, J.M. Grace, D.J. Miller, D.B. McDonald, K.E. Gray, M. Reiten, M. Ascolese, and H. Latvakoski, *IEEE Trans. on Mag.* **27** (2), 1219 (1991).
3. J.M. Grace, D.B. McDonald, M.T. Reiten, J. Olson, R.T. Kampwirth, and K.E. Gray, *J. Appl. Phys.* (1991) (to be published in the October 1 issue).
4. J.J. Cuomo, R.J. Gambino, J.M.E. Harper, J.D. Kuptsis, and J.C. Webber, *J. Vac. Sci. Technol.* **15** (2), 281 (1978).
5. S.M. Rossnagel and J.J. Cuomo, *Thin Film Processing and Characterization of High-Temperature Superconductors*, AIP Conf. Proc. No. 165, AIP, New York (1988), p. 106.
6. H.S.W. Massey, E.H.S. Burhop, and H.B. Gilbody, *Electronic and Ionic Impact Phenomena II*, Oxford, London (1969) pp. 1003-1050.
7. H.S.W. Massey, E.H.S. Burhop, and H.B. Gilbody, *Electronic and Ionic Impact Phenomena IV*, Oxford, London (1974) p. 2812.

FIGURE CAPTIONS

1. Dependence of deposition rates of Bi-Sr-Ca-Cu-O cations on position for a composite-target, magnetron-sputtered film. Deposition rates are normalized to their values at the point farthest from the central axis of the magnetron. The film was grown on MgO at 700 °C in roughly 20 mTorr of argon and 0.4 mTorr of oxygen. The MgO substrates were positioned on a heater block 2 inches from the target surface. Whereas Sr ($\diamond$), Ca ($\square$), and Cu ($\triangle$) exhibit higher rates nearer the magnetron axis (as expected), Bi ($\bullet$) shows a substantial drop in deposition rate toward the center of the magnetron, indicative of a preferential resputtering effect.
2. Schematic of magnetron apparatus. A sketch of potential vs. position is shown in the lower diagram.
3. Effect of oxygen partial pressure on deposition rates of Bi-Sr-Ca-Cu-O cations. Films were made at 700 °C. The deposition rates for Bi ($\bullet$) and Sr ($\diamond$) have been normalized to those for an ambient film. Because Cu, Ca, and Sr exhibit similar behavior, results are plotted for Bi and Sr only.

4. Effect of ozone partial pressure on deposition rates of Bi-Sr-Ca-Cu-O cations. Films were made at 650 °C. The deposition rates of Bi (●) and Sr (◇) have been normalized to their respective values in an ambient film. Because Cu, Ca, and Sr exhibit similar behavior, results are plotted for Bi and Sr only.

5. Effect of -40 V bias and ozone on bismuth content of magnetron-sputtered Bi-Sr-Ca-Cu-O Films. The graph indicates bismuth content of films grown with no bias at 650 °C(○), with -40 V bias at 650°C (●), and with -40 V bias at 690 °C(◆). Data are normalized to the bismuth content in an ambient film.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

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