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Deposition of BZO nano-sized dots on the substrate surface for the enhanced magnetic properties of superconducting films

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Abstract-- **Nano-sized dots have been formed on the buffered metal substrates using the novel approach of the electro-spray deposition, to modulate the substrate surface and induce the columnar defects in REBCO films grown on it. The $BaZrO_3$ precursor solution was synthesized and electro-sprayed out onto the negatively charged substrate surface. Using the electrostatic force, nano-sized dots can be grown and uniformly distributed on the buffered metal substrate. The height of BZO nanodots was observed above the 200nm, which are beneficial to induce the columnar defects onto the BZO as a seed. The density of BZO nanodots was also investigated and ~7.8/μm^2 was obtained. As the deposition distance of electro-spray was shortened there was ~8times increase of density of nanodots. The optimization of process variables in electro-spray deposition are discussed in respect to the superconducting REBCO films processed by the Metal-Organic Deposition with the effective flux pinning properties.**

1. INTRODUCTION

The higher critical currents in magnetic fields are of great interest for numerous electric power applications of the superconducting wire [1, 2]. In order to realize the enhanced in-field critical currents, it is highly required to prevent the motion of vortices inside superconductor, which can results in the electrical loss. The naturally existed defects such as dislocation, oxygen vacancy, are not enough to play such a role due to their lower density. So, introduction of artificial flux pinning sites through the processing routes are definitely considered to pin the moving flux lines [3, 4].

The artificial flux pinning sites should be designed carefully to maximize their efficiencies to get the high performance of the superconducting wire in the presence of magnetic fields. Two approaches are mainly tried for this purpose. The generation of artificial pinning sites inside the superconducting films is the direct method, which usually occur during the deposition of superconducting films itself [2-4]. The other approach uses the templates, which have the nano-sized dots on the substrate surface so as to induce the artificial pinning sites within the super conducting films on top of the nanodots as a seed [5].

Generation of flux pinning sites by growth of alternating multi-layers of YBCO 211 and YBCO 123 phase was successfully carried out and 2-3 times increase of the critical current density J_c at high magnetic fields was reported [3]. Also it was found that the incorporation of nano-particles such as $BaZrO_3$(BZO), $CaZrO_3$(CZO), and Y_2O_3 stabilized ZrO_2(YSZ) was performed and they form the extended columnar defects, which strongly pin the flux lines within the superconducting films, comprised of self-assembled columns of nanodots and nanorods [6]. The most significant progress is that the self-assembled columns can be extended from the bottom to the top of the ~3μm thick superconducting films with the high performance required for the practical applications [2].

Approach based on the surface-modulated templates was demonstrated using the silver nanodots by the rf-sputtering method prior to the superconducting film deposition. Ag nanodots formed for 3-5s were identified to have the 10-20nm(diameter) and up to 5nm(height) and proved to be effective in generating the artificial pinning sites with the increase of J_c more than one order of magnitude in magnetic fields [5].

Recently, chemical solution methods have shown to be very promising candidates to fabricate not only the superconducting layer but also the buffer layers to realize the cost-effective processing for the commercialization of superconducting coated conductors [7, 8]. These methods

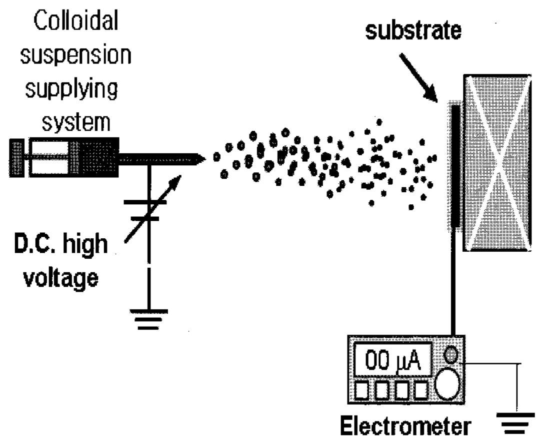

Fig. 1. Schematic diagram of electro-spray deposition.

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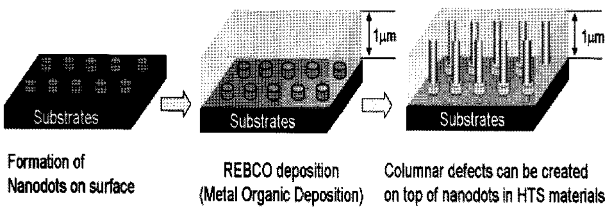

Fig. 2. Schematic illustrations of this research. (a) Formation of nanodots using electro-spray deposition, (b) REBCO deposition (Metal Organic Deposition), and (c) columnar defects can be induced on top of nanodots in HTS materials.

were also applied and proved its feasibility to generate the flux pinning sites within the superconducting films quite comparable to the expensive physical vapor deposition described above. Both the direct approach using the dispersion of nanodots incorporated in the solution of metal organic deposition and the indirect one using the modulated templates fabricated by chemical methods, demonstrated the generation of flux pinning sites within the superconducting films and their in-field J_c improvements [4, 5].

In this work, the formation of nanodots on the substrate surface using the chemical methods is presented. The size and density of the nanodots are investigated and the optimization of nanodots is discussed with the flux pinning properties of the superconducting films grown on it.

2. EXPERIMENTAL

The nano-sized dots have been formed on the buffered metal substrates with the architecture of Ni-5%W /Y_2O_3 /YSZ/CeO_2 (Ni-5%W/YYC). On the biaxially textured metal substrates, the first ~100nm thick Y_2O_3 buffer layer was grown epitaxially as a seed layer and followed by the ~150nm thick YSZ layer for the diffusion barrier and subsequent capping layer of ~200nm thick CeO_2. All the buffer layers have been grown epitaxially on the bi-axially textured substrate using rf-sputtering method [9].

Fig. 1 shows the schematic diagram of electro-spray deposition used to form the nano-sized dots on the buffered metal substrates. The BZO precursor solution passing through a nozzle was transformed to the plume of droplets electrically charged to a high positive voltage. Then, the fine continuous mist of droplets flied rapidly toward the negatively charged substrates. The charged particles of BZO precursor underwent the annealing process under the controlled atmosphere to remove the organic solvent, thus leave the nano-sized BZO dots on the surface [10].

The concentration of BZO precursor solution and deposition time of the electro-spray was varied to manipulate the size and density of the nanodots. The distance between the end of the nozzle and the surface of the buffered metal substrate was an important parameter in electro-spray deposition. To get the uniform mist of electro

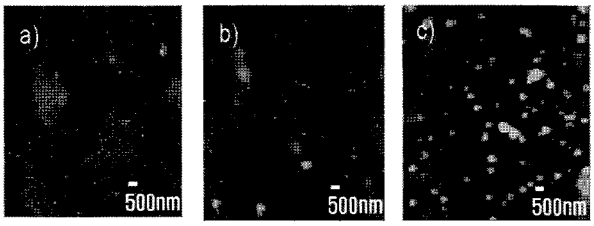

Fig. 3. AFM observation of $BaZrO_3$ nanodots processed at different concentration of precursor solution; (a) 50 times diluted, (b) 10 times diluted, and (c) original one.

-sprayed droplets, the shape like a cone-jet should be formed in front of the nozzle and was monitored using the charge coupled device (CCD) during the deposition. The formation of nanodots was studied by Atomic Force Microscopy (AFM) to reveal their size, density, and shape.

3. RESULTS AND DISCUSSION

There are lots of pinning sites to pin the magnetic flux lines entered into the superconducting materials in order to increase the critical current in the presence of magnetic fields. The columnar defects perpendicular to the substrate surface can provide the strong pinning sites to fields applied parallel to it. The naturally existing columnar defects were not enough for the practical applications of superconducting coated conductors. The generation of columnar defects composed of self aligned BZO nanodots or nanorods is of significant achievement which means that two different phases of materials can be deposited and controlled to be grown with its own direction separately and simultaneously [1, 6].

The indirect method was investigated using the template comprised of nano-sized dots on the buffered metal substrates which can be used as a seed to induce the columnar defects on top of it. Fig. 2 shows our strategy well. BZO was chosen as a candidate so as to match the materials used in MOD process which have the BZO nanodot dispersed inside. One of the advantages is that both formation of nanodots and MOD process are based on chemical solution deposition and easily combined to produce the coated conductors continuously.

BZO nanodots have been formed on YSZ single crystal buffered CeO_2 by rf-sputtering method. However there were rare dots found after the heat treatment in contrast to the ZrO_2 nanodots with ~6/μm^2 density on the same substrates. Surprisingly, it was possible to get the BZO nanodots of ~8/μm^2 density on the buffered metal substrates with the architecture of Ni-5%W/YYC. Because both templates are terminated with CeO_2 layer, it is speculated that the surface morphologies of CeO_2 layer are attributed to the formation of BZO nanodots in this situation. Also, the physical or chemical reaction can play an important role between them and further detailed study in microstructural investigation will be needed to clarify the mechanism [7].

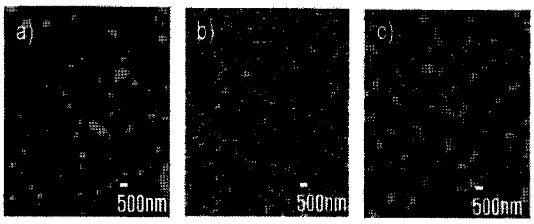

Fig. 4. AFM surface images of BZO nanodots electro -sprayed at different distance between the nozzle and substrates. (a) original one, (b) 40% shortened, and (c) 80% shortened.

The density change of BZO nanodots was detected when the concentration of precursor solution was varied as shown in Fig. 3. Here, other processing parameters like the injection rate of the solution, the distance between the end of the nozzle and substrate, and deposition time, etc were controlled to be constant within the manageable limits. The change of density from ~$0.6/\mu m^2$ (Fig. 3b) to ~$1/\mu m^2$ (Fig. 3c) was observed when the concentration was varied higher about 10 times. The main reason of dilution was to decrease the diameter of dots and there was change in diameter observed by AFM surface images from ~800nm (Fig. 3c) to ~400nm (Fig. 3b). The Fig. 3a was diluted further about 5 times compared to the Fig. 3b and ~$0.6/\mu m^2$ was obtained. In this case, however, the cone-jet was not formed accurately in front of the nozzle of syringe as displayed by the charge-coupled device [10].

To increase the density of nanodots, the distance between nozzle and substrate was varied with keeping constancy within the acceptable ranges for the other parameters. Because it should be noted that the formed cone-jet was influenced by the injection rate of the precursor solution, the applied high voltage, and solvent. So, when the distance changed, the voltage drop must be manipulated to maintain the shape of cone-jet for the generation of the mist of precursor droplet in electro-spray deposition. Fig. 4 shows the surface AFM image of BZO nanodots formed on YYC buffered metal substrates. It is clearly notified that the density of nanodots increased from ~$1/\mu m^2$ to ~$7.8\ /\mu m^2$ as the distance was 40% shortened. But the density decreased to ~$5.7/\mu m^2$ when the distance was further shortened to 80% of original one.

As shown in cross section analysis of AFM image(Fig. 5), the direction of the nanodots seem to be not parallel to the substrate normal and tilted about 15 degrees. The further detailed study for that is underway. If it is possible to control the direction of the nanodots on the substrate surface, it is highly advantageous to have the higher critical currents independent of the direction of the applied magnetic fields. And the height of the nanodots reached as high as ~562nm and this is the about half the normal thickness of REBCO superconducting layer.

To demonstrate the effectiveness of the nanodots fabricated by electro-spray deposition, A superconducting layer will be deposited and its flux pinning properties will be investigated in the future. Also, we try to reduce the dia-

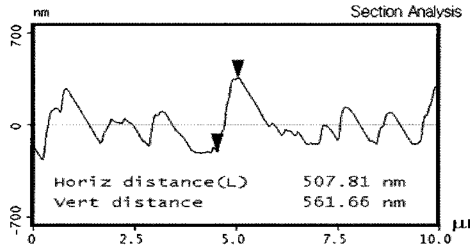

Fig. 5. Cross-section analysis of BZO nanodots on the buffered substrate as shown in Fig. 4c.

meter of the nanodots and will study the correlation between the diameter of nanodots and the flux pinning sites induced inside the superconducting layer.

4. CONCLUSIONS

BZO nano-sized dots have been deposited on the buffered metal substrates and the size and shape of the nanodots were observed using AFM. The change of the diameter from the ~800nm to ~400nm was done when the concentration of precursor solution was 10time diluted. The ~8 times increase of the density of BZO nanodots was possible through the control of the distance between nozzle and substrates. Also, it was found that the direction of the nanodots can be tilted by changing the process parameters and it can be highly valuable for obtaining the higher critical currents independent of the applied magnetic fields and practical application like rotating machinery.

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