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REDUCED NONLINEARITY SUPERCONDUCTING THIN FILMS TO TRANSMIT AND RECEIVE APPLICATION

PHASE II

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14. ABSTRACT

Report developed under STTR Phase II contract for topic AF06-T014. At UES, we have used the modified TFA MOD approach to grow high quality YBCO films with high critical current density up to 5.0MA/cm^2 at 77K self-field. Intermodulation distortion (IMD) of these films has been measured at MIT Lincoln Laboratory. Possible degradation of YBCO films due to thermal cycling has been studied using different protection materials. The experimental results of IMD in HTS materials show that IMD is high at low power and average at higher powers. No clear correlation has been found between IMD and microstructure as well as growth condition. Based on the data of thermal cycling test, it is found that selected protective layers are very effective in maintaining the properties of YBCO films.

15. SUBJECT TERMS

STTR Report, High T_c Superconductor, Yttrium Barium Copper Oxide, Intermodulation Distortion, YBCO, Metalorganic Deposition, TFA-MOD

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FOREWARD

This final technical report was prepared by Yongli Xu, UES, Inc., 4401 Dayton-Xenia Road, Dayton, OH 45432. The work was initiated under Air Force Office of Scientific Research (AFOSR) project monitored by Dr. Harold Weinstock, Arlington, VA 22203. The report covers work performed in-house at UES's Surface Engineering Laboratory and at MIT Lincoln Laboratory under the direction of Dr. D.E. Oates during the period 15 November 2007 – 13 November 2010.

1.0 SCOPE

This STTR Phase II project is directed towards the development of high performance large-area thick YBCO films and microwave devices on suitable single crystal substrates through modified TFA-MOD approach for transmit and receive applications. This project is subcontracted to MIT Lincoln Laboratory. We proposed to continue our success in Phase I to further increase critical current density of Jc to 3-5 MA/cm^2 and lead to state-of-the-art IMD (intermodulation distortion) by improving linearity, reducing surface resistance and increasing power handling capability of YBCO films. MIT Lincoln Laboratory is responsible for the characterization of non-linearity and intermodulation distortion. The major focus for UES is to develop high performance YBCO films with Jc greater than 3 MA/cm^2 at 77K self field by modified TFA-MOD process through coating, pyrolysis, and crystallization. To achieve these goals, layered growth mode is suggested and pursued by the control of driving force and HF saturation of precursor.

The UES approach would make film fabrication much cheaper, highly reproducible, and easy to scale up. The process was scaled up to make large area thick YBCO films for fabricating large arrays of microwave filters for the transmit and receive applications for both military and civilian applications

2.0 INTRODUCTION

High quality HTS (high-temperature-superconductor) thin films, in particular, the $YBa_2Cu_3O_{7-\delta}$ (YBCO, Y123) films, opened the new field for electronics. However, YBCO filters are limited in the power that can be passed through, which limits such filters to receive only applications. Nevertheless, even in low power receive applications the filters can produce intermodulation distortion (IMD). The origins of the limited power handling and the IMD are the same: the nonlinear nature of the surface impedance. Thus how to improve the quality of the HTS film has confronted researchers in this field for more than twenty years. At UES we used the modified TFA MOD approach to grow high quality YBCO films and high critical current density up to 5.0MA/cm^2 at 77K self-field. While the relationship between linearity and critical current density is still unclear and we have to tune the processing conditions to improve linearity of YBCO films even though its DC Jc is very good. On the other hand, for device application thermal cycling test is directly associated with the application requirements. Thus we have conducted thermal cycling test up to 1100 times between room temperature and liquid nitrogen temperature of 77K.

3.0 MAJOR ACTIVITY AND ACCOMPLISHMENT

The objectives of the research tasks were to qualify the YBCO films developed in this research that can be used for the device applications. The measurements of non-linearity and thermal cycling tests are directly associated with the application requirements and were performed in this Phase II. UES has developed high quality YBCO films using modified TFA approach with critical current densities of 5.0MA/cm^2 and greater at 77K self-field and the results have been reported in detail in Phase I final report. Selected YBCO films have been sent to MIT Lincoln Laboratory for IMD measurements and results have been reported in Phase I final report. Since then, two new samples designated as cc020209 and cc021309 have been prepared and sent to MIT for measurements. These samples showed critical current densities (J_c) of 3.0 and 3.2 MA/cm^2 respectively (Figure 1). Figure 2 shows the in-field J_c for the same samples.

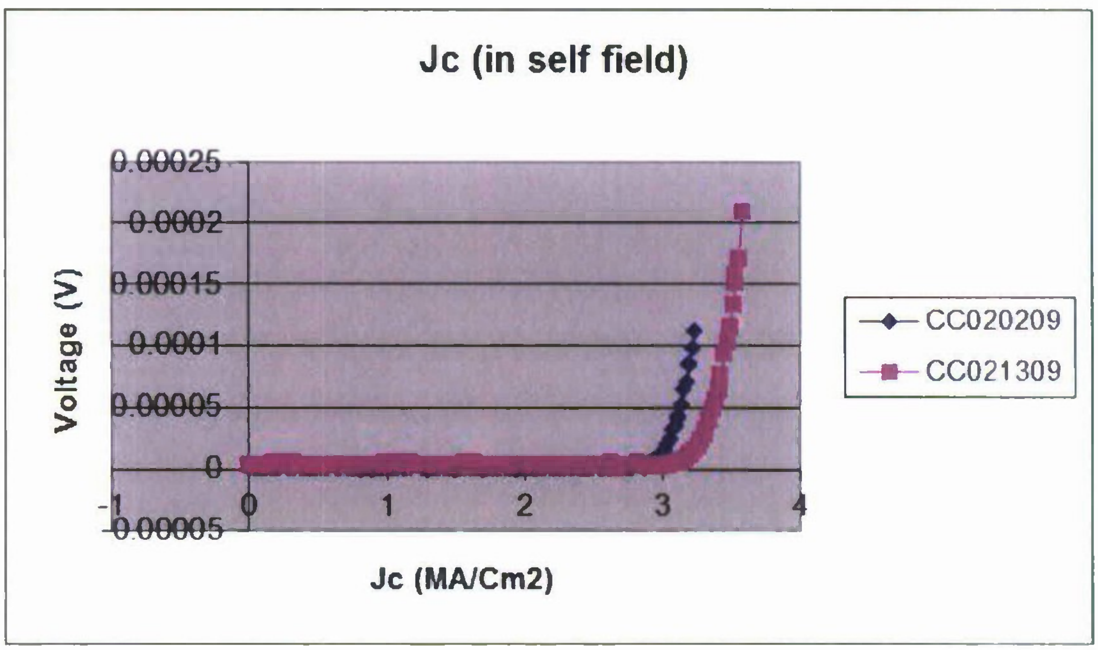

Figure 1. Critical current densities (J_c) of cc020209 and cc021309 samples in self field

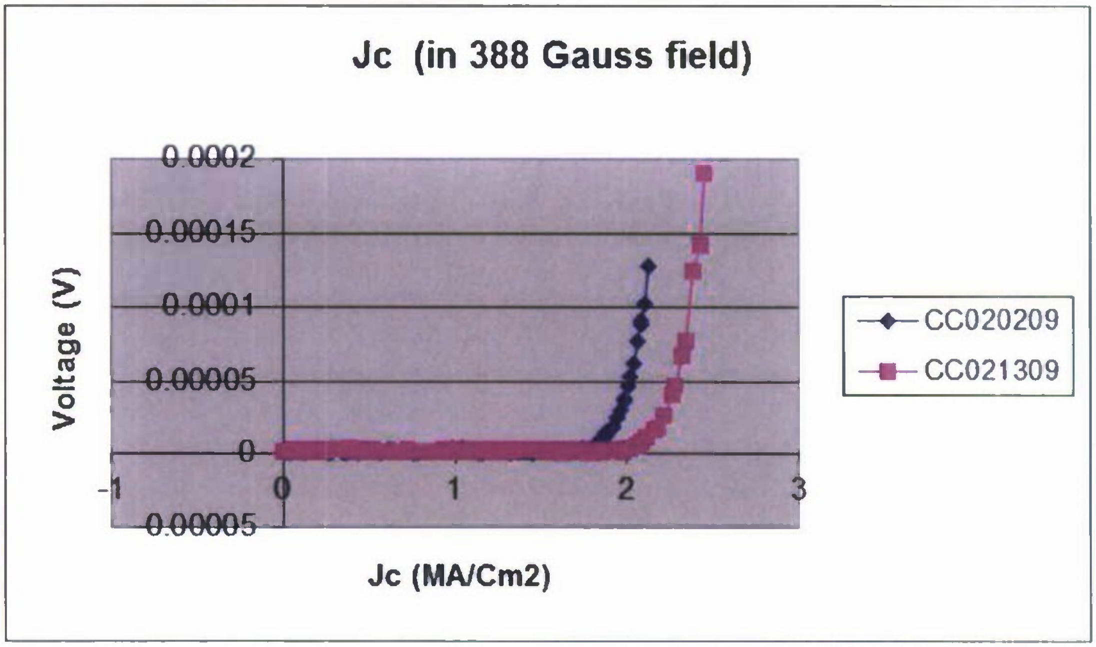

Figure 2. Critical current densities (J_c) of cc020209 and cc021309 samples in 388 Gauss field

3.1 MEASUREMENTS OF IMD

We performed IMD measurements on sample cc020209 and cc021309. The plots (Figures 3 and 4) show the IMD data for these samples compared with earlier samples at 50 K and 10 K. As we can see, sample cc020209 is among the best group but is not the champion one. While for sample cc021309, at low power the IMD of this sample is high relative to the other samples but at high power it is getting close to the average. Plots of surface resistance Rs and surface reactance ΔXs vs. circulating current in the resonator are also included as shown in Figures 5 and 6. They show that at low current there is a sharp rise in both quantities. At higher currents, the change in Rs and Xs is more gradual.

These plots explain why the IMD is high at low power and average at higher powers. We believe that the sharp rise in Rs and ΔXs at low power is due to very weak links in the sample, possibly from impurity and misaligned grain boundaries. These are saturated eventually and then the Rs and ΔXs look somewhat normal. If we could get rid of these weak links the performance would improve significantly.

Also, we notice in looking at the IMD data that the distribution seems bimodal. That is there are two clusters of curves. Perhaps understanding why there are these two groups of samples that behave like this, one could gain some insight on how to improve performance and get closer to the intrinsic values.

The experimental results show that from theoretical stand point, the understanding of IMD in HTS materials, the relationship between IMD and microstructure as well as growth condition is limited. More experiments are needed to build the model and clarify some basic principles.

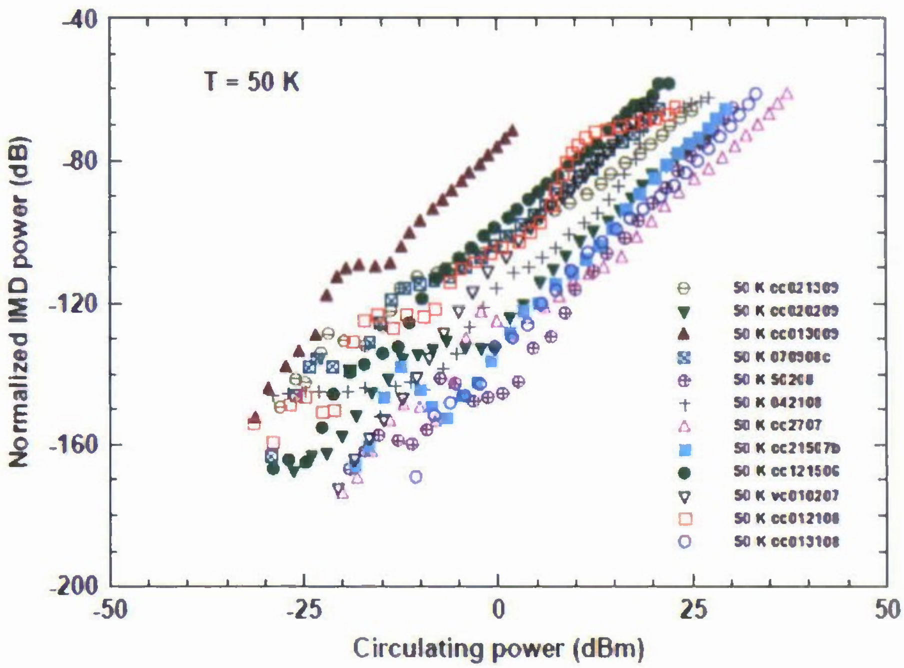

Figure 3. Intermodulation distortion (IMD) measurement showing improvement of IMD by nucleation and microstructure control. Measurement was performed at 50K.

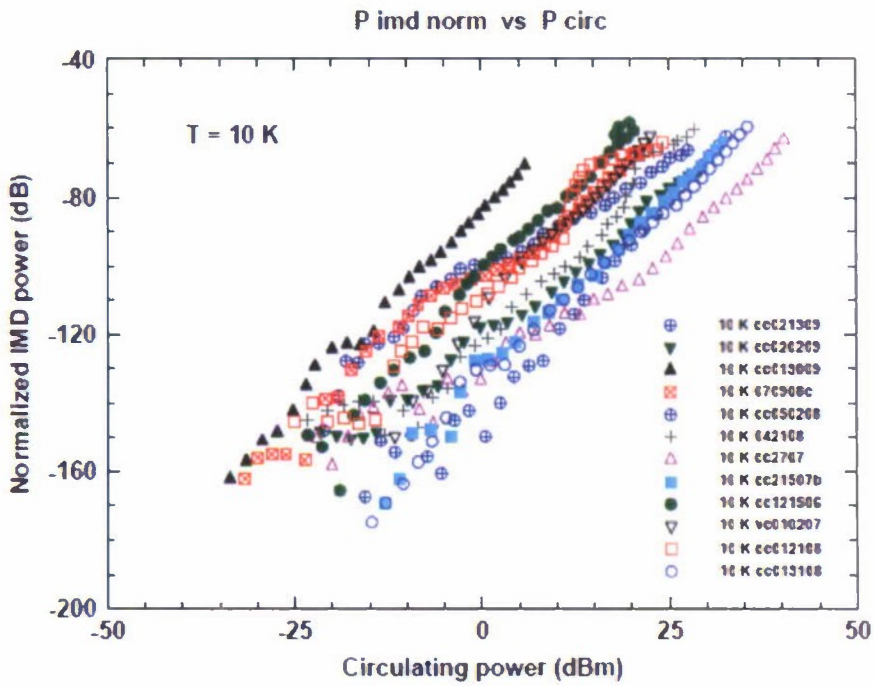

Figure 4. Intermodulation distortion (IMD) measurement showing improvement of IMD by nucleation and microstructure control. Measurement was performed at 10K.

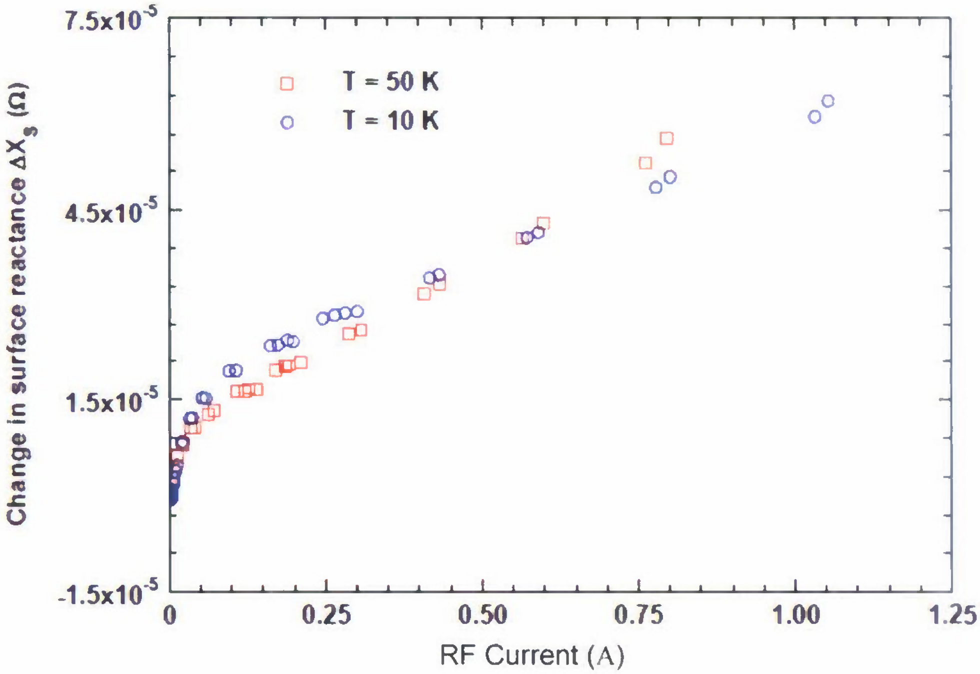

Figure 5. Measurements of change in surface reactance ΔXs vs. RF circulating current in the resonator at 10K and 50K respectively.

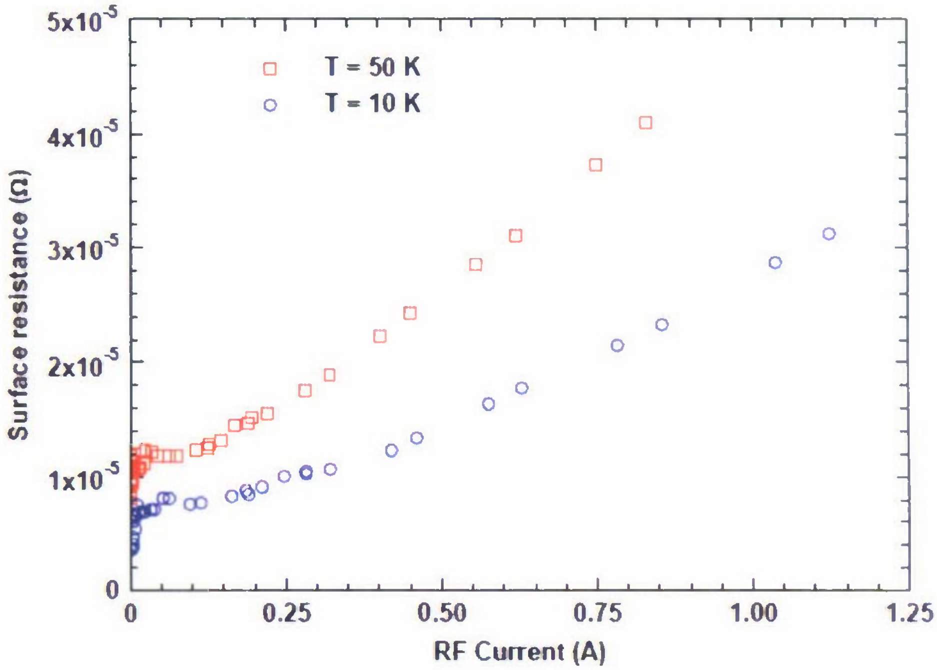

Figure 6. Measurements of surface reactance vs. RF circulating current in the resonator at 10K and 50K respectively.

3.2 THERMAL CYCLE TEST ON MOD YBCO FILMS

Thermal cycling test was performed in the Phase II research. The test was conducted between the boiling point of liquid nitrogen and room temperature. The transition time was precisely controlled. The material performance has been carefully evaluated after different thermal cycle times. Different protective materials have been explored and compared. The experiments were very well managed.

Experiment Set Up

Thermal cycling experiment was performed in the liquid nitrogen Dewar as shown in Figure 7. A special heated copper tube was mounted into the Dewar plug. This copper tube plays as temperature housing to warm the sample up to the designed temperatures. In the current experiments we heated the copper tube to a temperature of about 300K. It can also be heated to a higher temperature for other experiments. The sample with or without a protection layer was connected to a fishing line which can set the sample into liquid nitrogen or pull it out into the temperature housing of copper tube. The position of sample in the temperature housing was marked for the temperature consistency. It turned out that the sample cooling down was very fast (in seconds). We usually keep the sample in the liquid nitrogen for 1 min then moved it into the temperature housing for warm up. Warm up takes relatively longer time because the sample only hangs in the temperature housing without good thermal contact with the copper tube wall. We used longer time for warm up to reach temperature equilibrium.

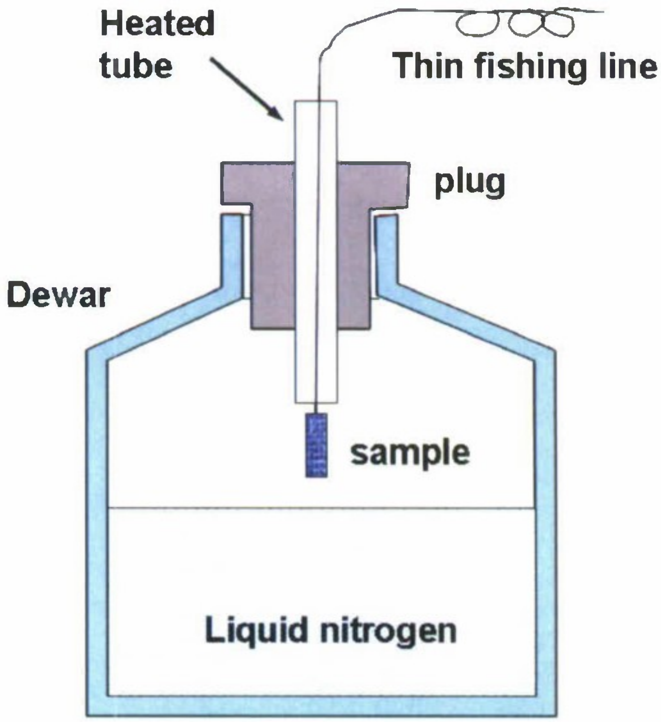

Figure 7. Thermal cycling experiment setup in the Liquid Nitrogen Dewar

Sample Preparation and Thermal Cycling Experiment

For the thermal cycling test, we used standard bridged samples for this research. The plan view of the sample is shown in Figure 8. Typically we made a narrow bridge on the YBCO film and the width of the bridge is about 600 μm. we put silver contacts for current and also for the voltage as shown in the setup. We tested sample with or without a protection layer and looked into the effect of the protection.

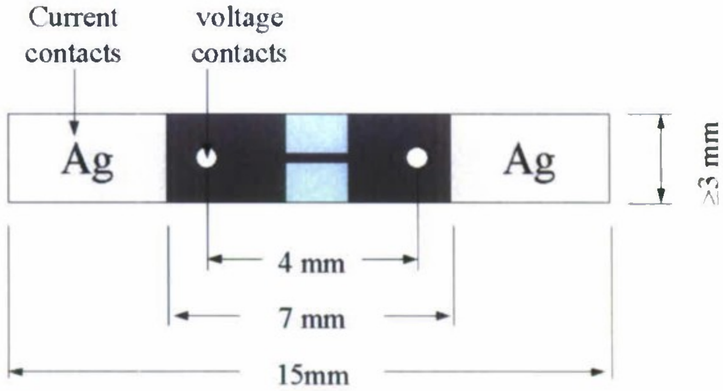

Figure 8. Standard bridged YBCO samples for the thermal cycling test

The thermal cycling experiment was performed in-house at UES Inc. We were working on four samples with different protective layers. The first two samples had no protection. We ran 100 times thermal cycling on these samples and degradation was observed on one of them but very minor effect on the other one. The third sample was protected with plastic film. We have run and tested at 100 times, 200 times, and 300 times. With the plastic thin film protection no degradation was observed after 300 cycling. The last sample reported in this research was a sample protected with a silver layer of about 0.5 μm. After the thermal cycling of 100 times, rather than degradation of the sample performance (Jc), some increase was observed. It will be interesting to perform further thermal cycling test on this sample.

In this report period we finished all of the thermal cycling experiments using different protection layers. Thermal cycle tests on each of these protection materials have been carried out over 1000 times.

3.2.1 Using Organic Protection Layer

For the first set of experiments the sample was protected with organic thin film. The thin film was attached on the surface of YBCO film and then thermal cycle test was conducted. We tried different materials, for example, scotch tape and Cling wrap (for food wrap). There is not much difference as long as moisture was sealed out of the YBCO film. Figure 9 plots the properties of YBCO films under different cycling numbers protected by plastic thin films. This sample was measured at cycle numbers of 100, 200, 300, 400, 700, 1000, and 1100 times. Not much change was observed for these cycling numbers in particular for 1000 times without any treatment. The performance of this sample gets improved when treated in oxygen even after extra cycles were applied. About 10% increase was observed on the critical current density of Jc after 1100 cycles. The experimental data confirmed that the damage from thermal cycling (at least in the number range of this experiment) is very minor and can be neglected. This is further confirmed by the test in magnetic field as shown in Figure 10. The data for the in-field measurement show that in the cycling range of the experiment, rather than performance degradation, the in-field Jcs are getting improved. The improvement may come from pinnings that were introduced during thermal cycling. Appropriate pinnings can increase Jc in particular for those measurements in a magnetic field.

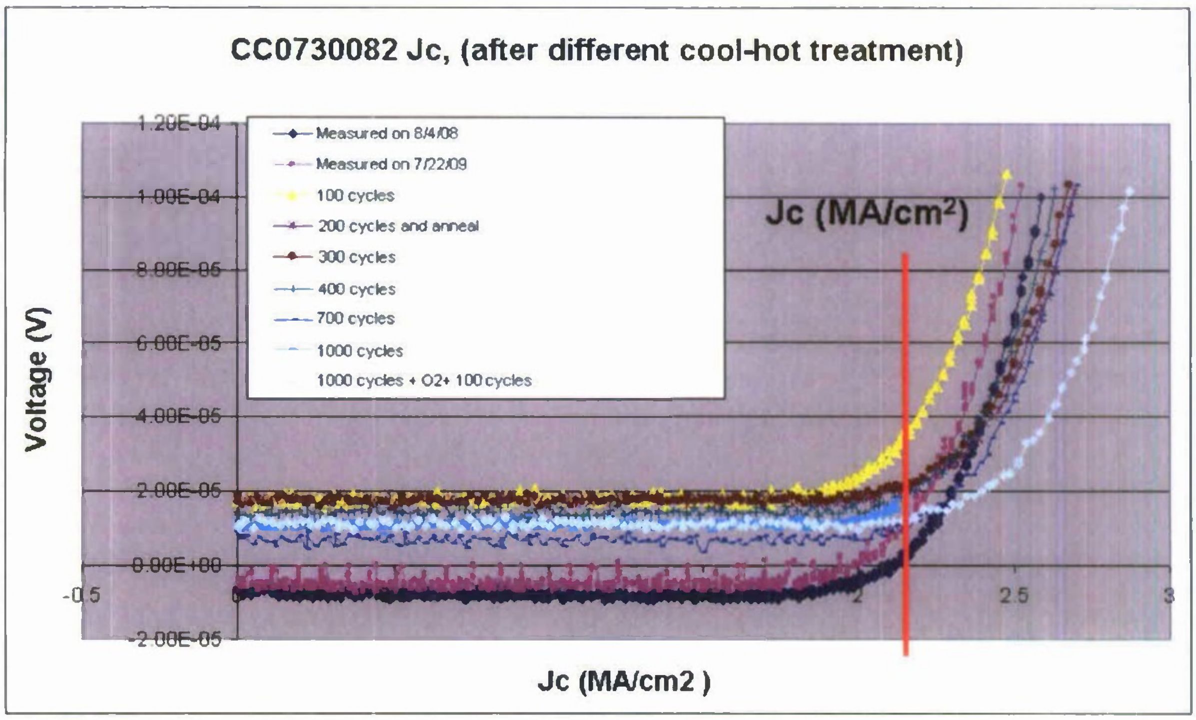

Figure 9. The Jc measurements under different thermal cycles, measured at 77K

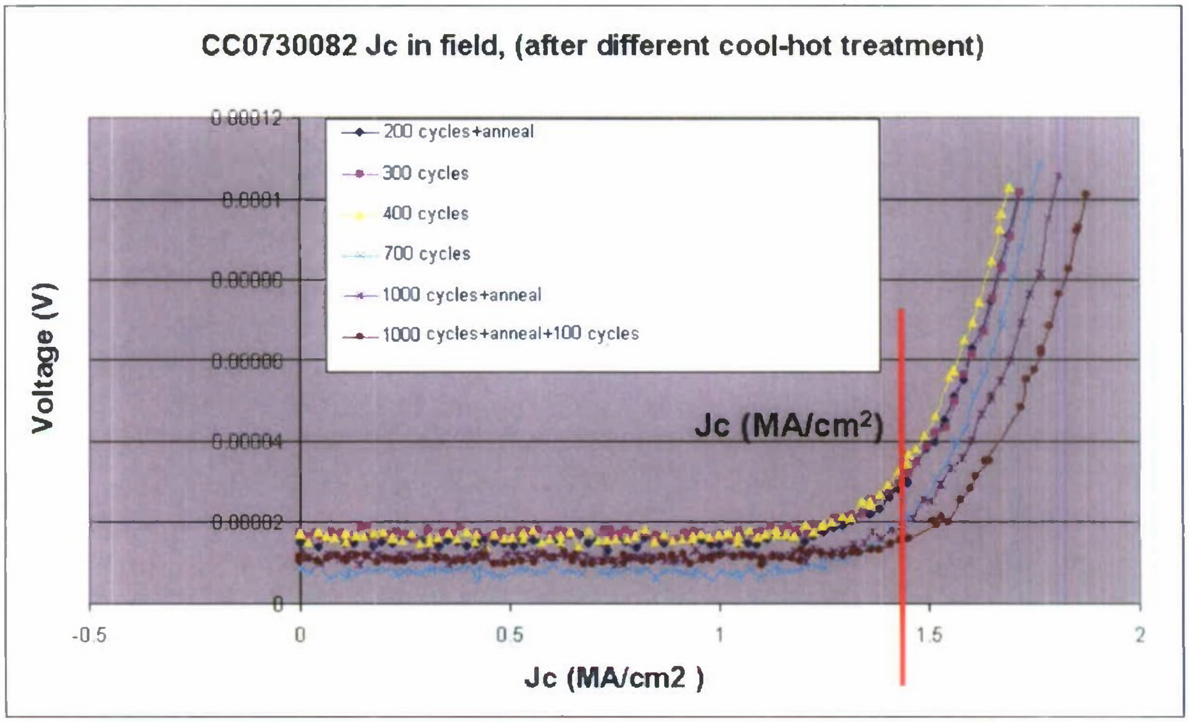

Figure 10. The Jc in-field measurements under different thermal cycles. Note, the experiments were performed at 77K and 388 Gauss

The data of the in-field measurements are consistent with that in self field. Improvement was observed for high cycling numbers such as 700, 1000, and 1100 times. It seems that Jc improvement is because of the cycle number. The Jc difference between 1000 and 1100 times indicates that oxygen treatment may play some role for the Jc increase. All the experimental data are consistent and we do not anticipate any side effect for the YBCO films on the performance of device.

3.2.2 Using Silver Protection

For the second set of experiments the sample was protected with silver thin film of about 0.5 μm. Silver protection on the YBCO films was widely used in other applications, for example in coated conductors. Silver layer can play the role of protection as well as metal contact, both of which are very important for device application. Silver thin film was deposited onto YBCO film by magnetron sputtering. Thermal cycle test followed the Ag sputtering and anneal.

Figure 11 plots the properties of YBCO films with silver protection layer under different cycling numbers. This sample was measured at cycle numbers of 100, 200, 500, 800, 1000, and 1100 times. Not much change was observed for these cycling numbers even for 1100 times. We found some difference of Jc measured on 09/12/2008 and 07/29/2009. This happens all the time because the sample was stored in humid air with no protection for about 320 days. This would not happen if the samples were protected or stored in the dry environment for example in a desiccator.

Once the sample was silver coated and annealed then it becomes robust for environment and thermal cycling test. As shown in Figure 12 we see very minor change of Jc after the cycle number increased from 100 to 1100 times. This small change may also come from mechanical damage from thermal cycling test. Sometimes mechanical damage can be observed. Nevertheless the data consistency is still very good.

The data of the in-field measurements are consistent with that of the self-field. Improvement was observed for low cycling numbers from 100 to 500 times. About 10% increase was observed on the critical current density of Jc after 1100 cycles. The experimental data confirmed that the damage from thermal cycling (at least in the number range of this experiment) is very minor and can be neglected. The Jc improvement is not obvious for high numbers above 500 times. All the experimental data are consistent and we do not anticipate any side effect for the YBCO films to be used for the device fabrication.

The in-field Jc improvement may come from the pinnings that were introduced during thermal cycling.

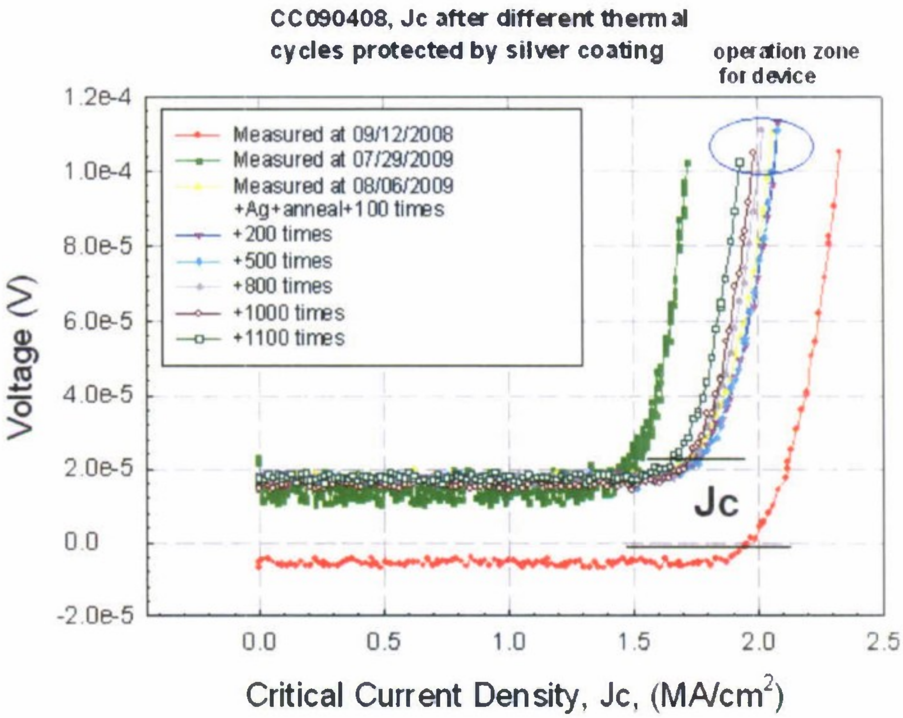

Figure 11. The Jc measurements under different thermal cycles, measured at 77K

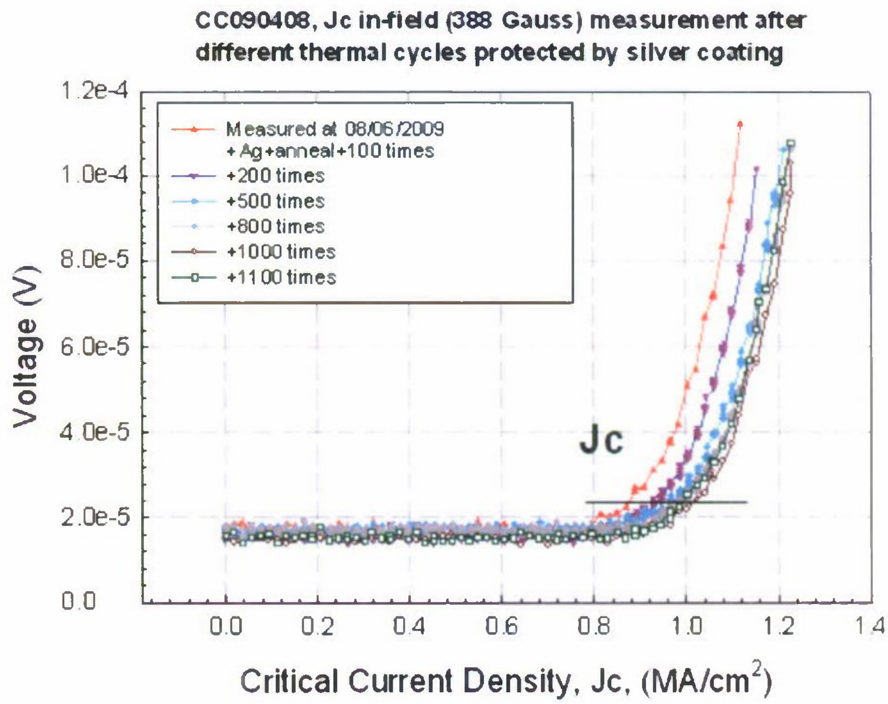

Figure 12. The Jc in-field measurements under different thermal cycles. Note, the experiments were performed at 77K and 388 Gauss

3.2.3 Using Oxide (Y_2O_3) Protection

For the third set of experiments the sample was protected with oxide thin film of about 0.5 μm. Here we chose Y_2O_3 is because it matches with YBCO very well. Usually Y_2O_3 is used as one of the buffer layers for YBCO epitaxial growth in coated conductor fabrication. Yttrium is the component of YBCO and sometimes it is used for pinnings as well. Thus selection of Y_2O_3 is for its positive effects in this application. Other oxide like CeO_2 can also be a good candidate for the similar reasons.

Oxide layer is dense and can protect the sample from mechanical damage; in particular it can seal YBCO from moisture, the killer that causes degradation. Y_2O_3 thin film of about 0.5 μm was deposited onto YBCO film by magnetron sputtering. Thermal cycle test followed the deposition and anneal. Figure 13 plots the properties of YBCO films with Y_2O_3 protection layer after different number of cycles. This sample was measured at cycle numbers of 200, 620, and 1000 times. Not much change was observed for different cycling numbers after the Y_2O_3 deposition and anneal. As described previously, we found some property change between the measurement of 09/30/2009 and 12/30/2009. This happens all the time because the sample was stored in humid air with no protection. This would not happen if the sample was protected or stored in the dry environment for example in a desiccator. Once the sample was oxide coated and annealed then it becomes robust for environment and thermal cycling test. As shown in Figure 14 we see very minor change of Jc after the cycle number from 200 to 1000 times. This small change may also come from mechanical damage from thermal cycling test.

The data of the in-field measurements are consistent with that of self-field measurements. Very small improvement was observed. The experimental data confirmed that the damage from thermal cycling (at least in the number range of this experiment) is very minor and can be neglected. All the experimental data are consistent and we do not anticipate any side effect for the YBCO films to be used for the device fabrication in this research.

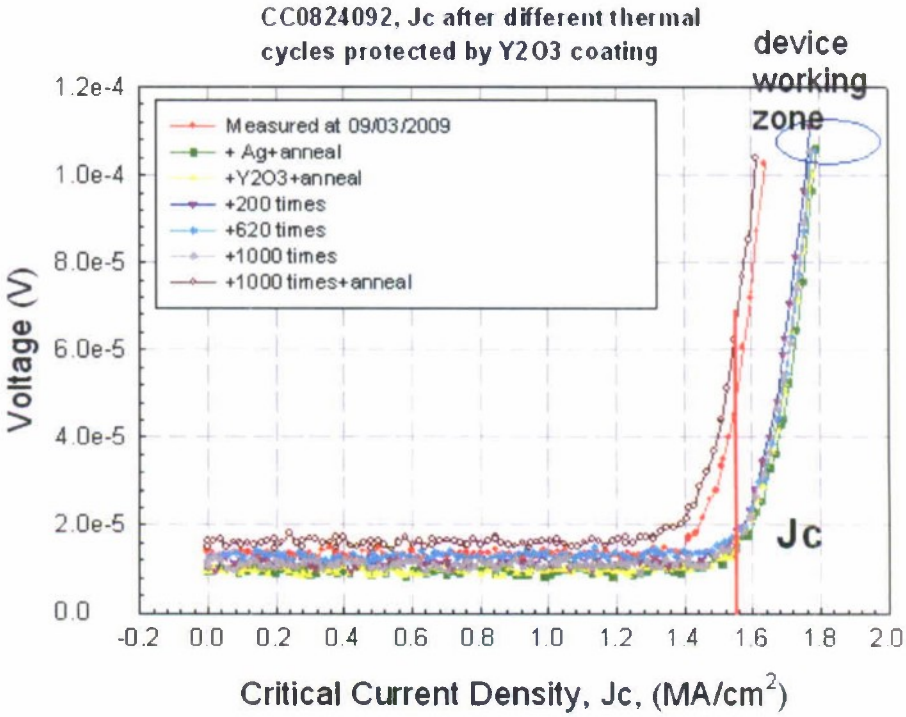

Figure 13. The Jc measurements under different thermal cycles, measured at 77K

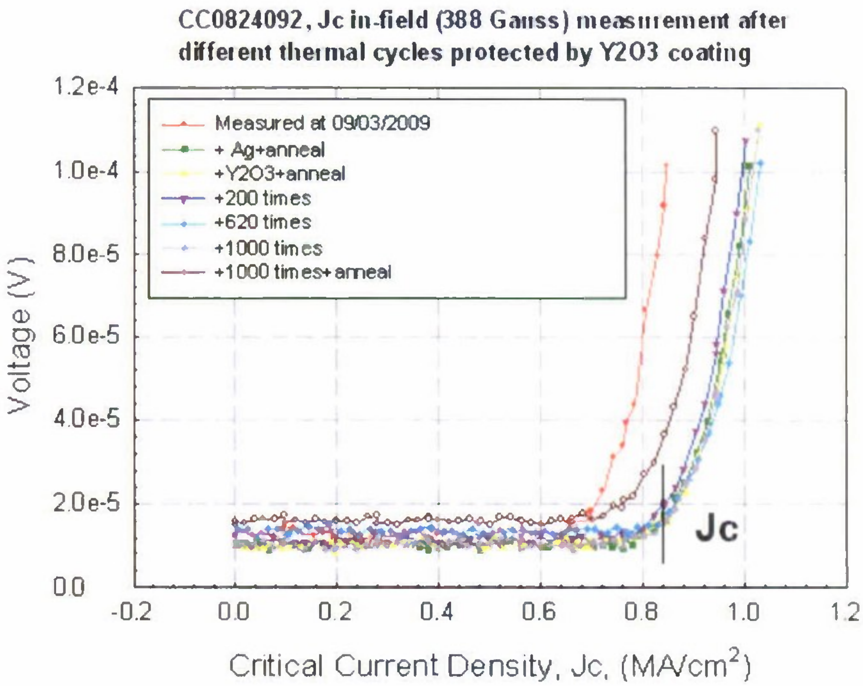

Figure 14. The Jc in field measurements under different thermal cycles. Note, the experiments were performed at 77K and 388 Gauss

4.0 DATA ANALYSIS AND DISCUSSION

The results on IMD measurements at MIT showed that IMD is high at low power and average at higher powers. This is related to the sharp rise in Rs and ΔXs at low power. We believe that this is due to very weak links in the sample, possibly from impurity and misaligned grain boundaries. These are saturated eventually and then the Rs and ΔXs look somewhat normal. If we could get rid of these weak links the performance would improve significantly.

The experimental data on protective layer discussed above show that YBCO film with a protective layer not only can attain its electrical properties but also have small improvement. Not much difference was observed among these protecting materials. All of the features are comparable for the different protecting materials. That means other materials can also be used for protection as long as they are able to block moisture from YBCO film and no reaction with YBCO at the operation temperatures.

In the previous section we compared the protective effect among different materials. To confirm the reproducibility we also did repeat experiment using the same protective materials of plastic and silver. Figure 15 shows Jc measurement for different thermal cycles up to 1000 times on another YBCO films protected with plastic material. The data reported on this sample is smoother than the previous one. We can see that there is almost no change on Jcs for various thermal cycling numbers. However, the data of in-field measurement (Figure 16) show about 10% Jc increment, indicating that pinning plays a role in this film. These results agree very well with that shown in Figure 9 and 10, which means the effect of protective layer is reproducible.

Another important feature that can reflect the quality of the YBCO film after thermal cycling is Tc measurement. We have done Tc measurement on samples after 1000 thermal cycles. The data are shown in Figure 17 and 18. The Tc data show that thermal cycling has almost no effect on normal state resistivity, transition temperature and transition width. It also shows that protection material has no effect on Tc transition for different thermal cycles. Based on the experimental data, the thermal cycle effect is obvious and no damage has been shown for the cycling number up to 1100 times. We anticipate there is no damage if the thermal cycling number is not too high. If we assume that the device based on YBCO sensor shut down every week, the current thermal cycles number can guaranty that the system has the life span of 20 years and more.

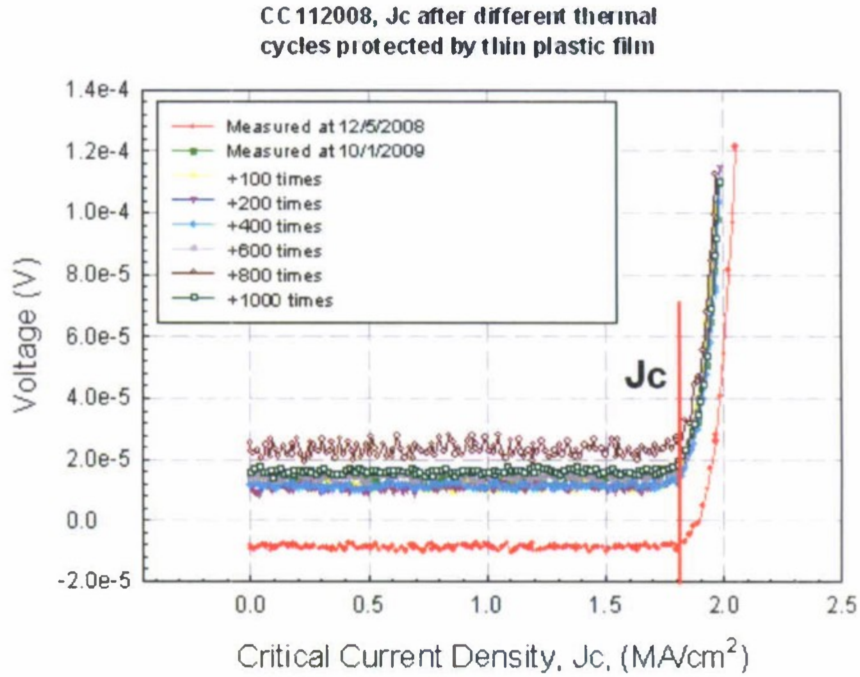

Figure 15. The Jc measurements under different thermal cycles, measured at 77K

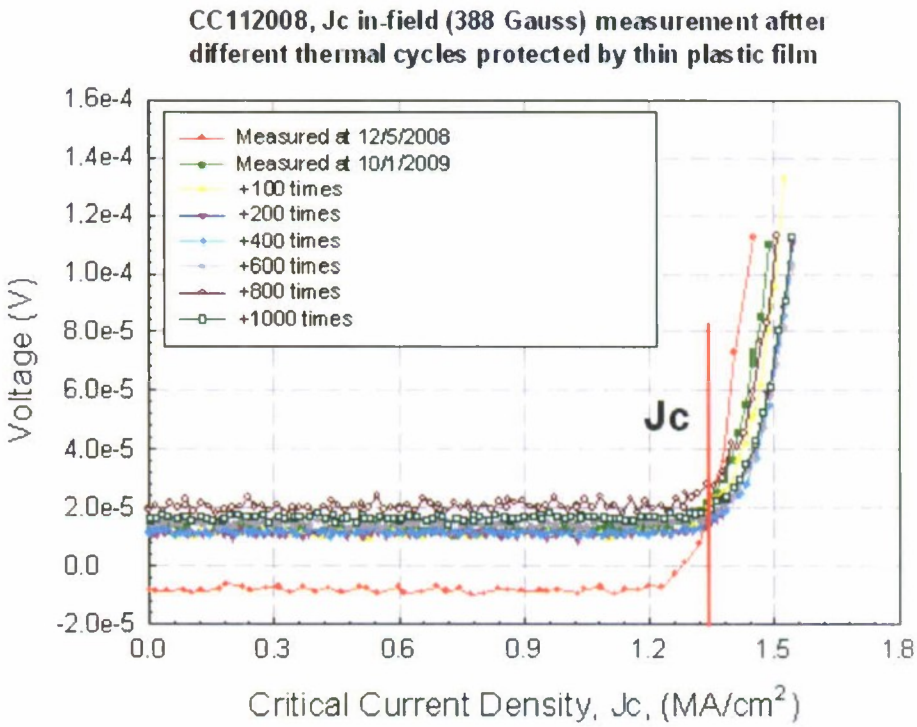

Figure 16. The Jc in field measurements under different thermal cycles. Note, the experiments were performed at 77K and 388 Gauss

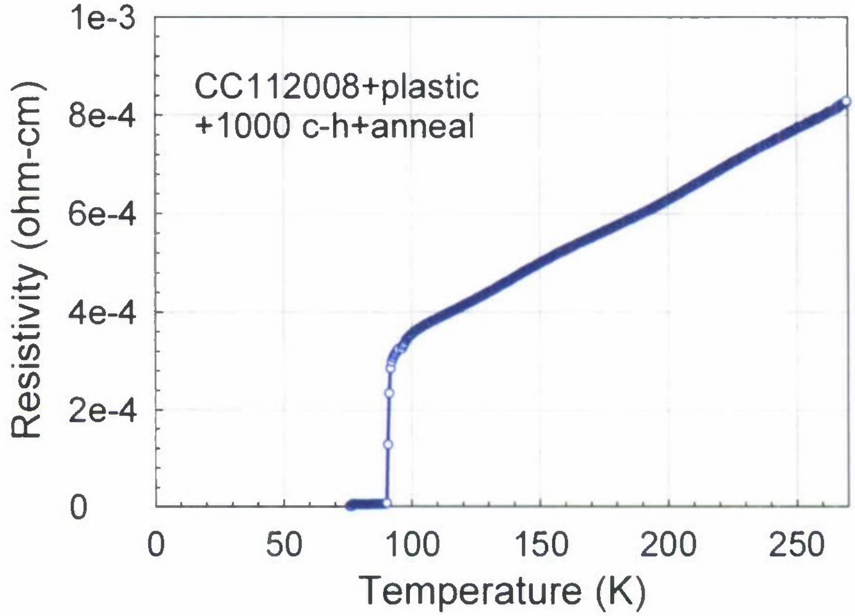

Figure 17. Four-probe transport Tc measurement after thermal cycles of 1000 times

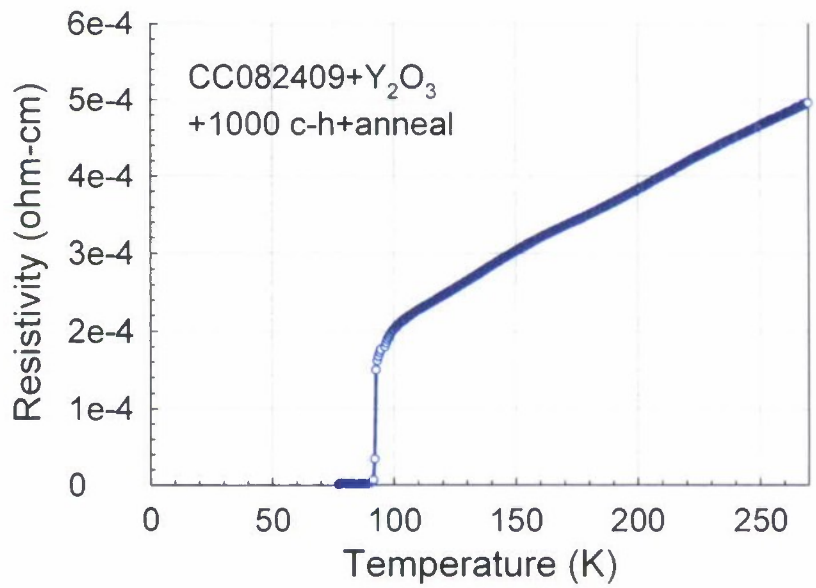

Figure 18. Four-probe transport Tc measurement after thermal cycles of 1000 times

5.0 SUMMARY

The experimental results of IMD in HTS materials show that the relationship between IMD and microstructure as well as growth condition is limited. More experiments are needed to build the model and clarify some basic principles.

Based on the data of thermal cycling test, it is found that the protective layer is very effective in maintaining the properties of YBCO films. Not much difference was observed among the protecting materials used. All of the features are comparable for the different protection materials. That means other materials can also be used for protection as long as they are able to block moisture from YBCO film and no reaction occurs with YBCO at the operation temperatures. Rather than degradation, a small Jc improvement has been observed.

Based on the experimental data, YBCO films do not show degradation on the thermal cycling number up to 1100 times. We anticipate there may not be any damage if the thermal cycling number is not too high compared with the test number in these experiments. Assuming that the device based on YBCO sensor shut down every week (that is one thermal cycle per week), the current thermal cycle's number can guaranty the system to have a life span of 20 years and more. This is very important for device applications