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# A Comparison of High-Temperature Superconductors in Multi-Chip Module Applications

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## Abstract

In the application of high-temperature superconductors (HTSCs) in multi-chip module (MCM) technology, it is first necessary to investigate the advantages and disadvantages of the various HTSC compounds. The standard criteria for comparing the suitability of HTSCs in electronics applications has been critical temperature ( $T_c$ ) and critical current density ( $J_c$ ). It is also necessary to consider the physical properties of HTSCs in relation to the various processing techniques required in fabrication of MCMs. These techniques can be grouped into four main areas: deposition, patterning, packaging, and characterization. The four main HTSC materials, Y-Ba-Cu-O, Bi-Sr-Ca-Cu-O, Tl,Ba-Ca-Cu-O and Hg-Ba-Ca-Cu-O, will be compared to determine which is most suitable for MCM application.

## Introduction

In the decades since the popular advent of the transistor in the 1960s, there has been continual and steady improvement in both the performance and cost of electronics equipment through miniaturization. This effort has given us the multi-chip module (MCM) as the latest and most promising technique to be introduced. MCM technology improves the speed at which devices can operate and decreases the power lost by eliminating as much length as possible from the interconnection between the individual devices. With this new technology some new barriers to increased speed and performance have arisen. By concentrating all of the devices in one area, the problems due to Joulean heating ( $I^2R$  losses) and electromigration are increased. Also, the lack of recent improvements may indicate that the upper limit of the speeds that can be expected from current semiconductor devices using conventional interconnects have been reached.

All of these problems can be addressed by combining high-temperature superconductors (HTSCs) with MCMs. Some of the interconnecting lines may typically carry 50 - 100 mA of current. Therefore, they account for a major portion of the heat generated (Burns et al., 1993). Replacing the lines with zero resistance HTSCs eliminates these  $I^2R$  losses. This means less heat and less power consumed. The refrigeration required for HTSC operation further limits the overall heat production to less than that produced by the individual devices. All of this allows for an even greater decrease in the interconnection lengths which, in turn, maximizes the operating speed of the MCM.

HTSC devices have been shown to be more than 2.5

times faster than their semiconductor counterparts, use three orders of magnitude less power, and do not suffer from electromigration problems (Van Duzer and Tuner, 1981). Their use in MCMs should produce the next quantum jump in performance. A cross-sectional schematic of an MCM is shown in Figure 1.

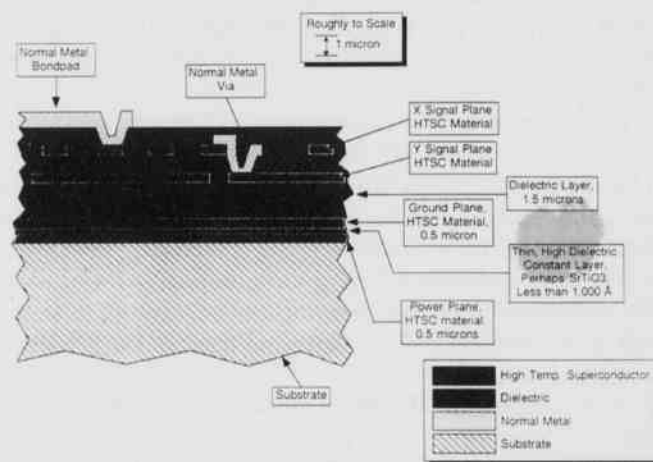


Fig. 1. Cross-sectional Schematic of a Superconducting Multi-Chip Module.

But, which HTSC offers the best overall prospects for MCM applications? This is the first question to be answered in the search for a viable superconducting MCM. When comparing HTSCs, the standard for suitability in electronics applications has been the materials critical temperature, ( $T_c$ ), and critical current density, ( $J_c$ ). It is

also necessary to consider the additional requirements and effects due to the different fabrication steps such as material deposition, patterning, packaging and characterization. This paper is the result of our research in each of these areas.

Using the initial criterion of  $T_c$ , a great number of HTSCs can be eliminated. The cost of cooling below liquid nitrogen temperature (77K) tends to preclude using HTSCs with  $T_c$ 's any lower. The currently viable HTSC materials with  $T_c$ 's above liquid nitrogen temperature can be separated in to four groups: yttrium-based, bismuth-based, thallium-based, and mercury-based. These four groups will be dealt with in this paper.

### Yttrium

There are at least three variations to the yttrium-based HTSCs with the only significant differences being the  $T_c$ s (40K, 80K, 90K) and the ease of production. Fortunately, the highest  $T_c$  (90K) belongs to the phase of yttrium material that is the easiest to produce.  $YBa_2Cu_3O_x$ , known commonly as either YBCO or 123, was the first material discovered to superconduct above liquid nitrogen temperature (Wu et al., 1989). This fact and the relatively low toxicity of the component materials seem to be the only really good characteristics that YBCO possesses.

An ongoing study by our group at the University of Arkansas indicates that to achieve an effective current density, a given HTSC must be held to 10 - 20% below its  $T_c$  (Ulrich, 1994). While this is better than the 30% or  $T_c/2$  values commonly accepted in the scientific community (Doss, 1989), it still puts YBCO at the very borderline for use with liquid nitrogen.

Most of the drawbacks encountered in the production of YBCO thin films can be tied to one problem. Due to critical mismatches in lattice parameters, it is difficult to get good epitaxial growth for YBCO on the viable low dielectric substrates in use today (Werder, 1991). This means that, no matter how good a deposition technique, YBCO films will tend to be comparatively rough in texture and have a limited  $J_c$  due to internal flaws in the achievable crystalline structure.

The deposition of YBCO on a substrate has typically been accomplished using off-axis sputter deposition. While this method can produce usable thin films, it is often necessary to anneal these films in an oxygen ambient at approximately 450°C after deposition in order to correct for oxygen depletion and to achieve an acceptable  $T_c$ . Fortunately, an on-axis method has been demonstrated that produces thin films with  $T_c$ s of 88K and  $J_c$ s of greater than  $10^6$  A/cm<sup>2</sup> with no post annealing required (Blue and Boolchand, 1991). It should be noted however, that the current density for this material is only  $10^4$  A/cm<sup>2</sup> at 77K just as for most YBCO films (Jin et al., 1988).

Another successful method for the deposition of YBCO has been demonstrated using metalorganic chemical vapor deposition (MOCVD) combined with rapid isothermal processing (RIP) (Singh et al., 1991). With  $T_c$ s of 89K and  $J_c$ s of  $1.5 \times 10^6$  A/cm<sup>2</sup> at 77K, this is by far the best method for producing YBCO films seen to date.

Pulsed laser deposition has also been used successfully to cover small areas, but this technique has proven to be a very costly and a difficult process to control (Burns et al., 1993). Laser deposition does seem to be an excellent choice for spot deposition of YBCO in applications such as individual connections between layers commonly called vias.

In the areas of patterning, packaging and characterization, there is another major drawback. YBCO has a very high affinity for water. When exposed to moisture, the properties of YBCO tend to degrade. This process is accelerated by flaws in the crystalline structure so common to current processing techniques. Another aspect of this fault is that YBCO tends to form an oxide skin layer. This means an added difficulty for any patterning process. Also, this creates a problem in making direct contact to YBCO films as is necessary for multilayer applications, metalization for packaging purposes, or just testing the material. With some small difficulty, this can be dealt with using a procedure consisting of a solution of bromine in methanol that will remove the skin layer (Vasquez et al., 1988). A non-superconducting surface layer can also be removed by brief exposure to a low-energy cleaning ion bombardment.

Yttrium-based HTSCs have been successfully etched using weak acidic solutions such as phosphoric, nitric and hydrochloric acids. However, YBCO's reactivity with the various substrates, while not notably greater than for other HTSCs, when combined with the noted skin effect creates a scum layer between the substrate and the YBCO thin film that seems impervious to these enchants.

Yttrium-based HTSCs can also be dry etched using either a reactive process with a halogen such as chlorine, or by argon ion milling. Both of these methods suffer from the same structural distortions found in deposition techniques. For the reactive process, it is necessary to either post-etch anneal or use a mask that can keep oxygen from escaping during the etching process. In argon ion milling, the problem can be solved by cooling the sample during the etching process, preferably with liquid nitrogen. But, since photoresist are often used for masking in both dry etching processes, the problem with moisture is still present.

### Bismuth

There are several different bismuth based HTSCs, with

the highest  $T_c$  being ~114K for  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ , but it is very difficult to produce the higher  $T_c$  phase of this compound (Bi 2223). This is due to the intergrowth of the Bi 2212 phase which has a  $T_c$  of 85K. Many attempts to enhance growth of the 2223 phase have been made with varied results (Endo et al., 1988; 1989; Tarascon et al., 1988; Huang et al., 1990). One procedure produces good thin films, but requires a heating period of one week (Sleight, 1988). The most promising method seems to be the addition of lead in the form  $\text{Bi}_{2-y}\text{Pb}_y\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$  to stabilize the  $T_c$ . This method has produced  $T_c$ 's in the usable range of 104 - 112K (Xin and Sheng, 1991). This is the most commonly encountered form of the bismuth compound and can be deposited using the same methods as described for YBCO. Most of the information gathered about the bismuth-based system has been for this lead mixed form. As other easily produced phases of the bismuth compound have lower  $T_c$ 's than YBCO, they are of little interest to the MCM field.

The addition of lead to bismuth HTSCs defeats one of the bismuth compound's major benefits. That is, the relatively low toxicity of the elements used. While the lead can be incorporated easily, it will still require special handling like the thallium and mercury compounds.

Most reports of  $J_c$ 's are somewhere above  $10^4$  A/cm<sup>2</sup> at 77K which is similar to YBCO (Doss, 1989). This is probably due, in part, to the difficulty in producing a pure phase of this material. The lattice parameters of the bismuth compounds, though not exact, are better matched to the low dielectric substrates than YBCO's. This would indicate better epitaxial growth and better  $J_c$ 's. Comparison of the thermal power properties also indicates this conclusion (Xin et al., 1992). Indeed, a 110K sample with a  $J_c$  of  $3.4 \times 10^6$  Z/cm<sup>2</sup> at 77K has been reported (Grenwald, 1991), but it should be noted that this sample did not contain lead and is not easily reproduced.

Bismuth-based HTSCs can be etched with the same methods as YBCO and slow none of the problems due to YBCO's affinity for moisture. Most forms of this compound appear to be fairly stable and much less brittle than YBCO. It should be noted that bismuth compounds require the same precautions for dry etching methods as YBCO, and although the etching damage is generally of a lesser extent, bismuth compounds can easily be destroyed during any annealing process.

Bismuth compounds have shown a tendency to flake in layers similar to mica (Doss, 1989). This could cause some slight problems in packaging, but should not prove to be a major concern.

The only problems with the characterization of bismuth based HTSCs are directly related to the ability to produce a pure phase material.

## Thallium

Like bismuth, thallium-based HTSCs exist in many different phases. Unlike bismuth, however, the highest  $T_c$  (125K) phase is relatively easy to produce.  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ , commonly referred to as Tl2223, has one major drawback. Thallium is a very toxic substance that can be absorbed through the skin. It can be absorbed over a period of time and is not normally purged from the body. Therefore, proper precautions must be taken when dealing with this material. Special precautions should be taken when working with lead or mercury. However, the precautions required for working with these materials are only slightly more than those normally observed in a conscientious production facility (Chelton et al., 1991). As these facilities are already dealing with arsenide, cyanides, and many other toxic compounds, the addition of thallium should present no insurmountable problems.

Excellent quality thin films of the 2223 phase have been deposited by several methods such as spin coating, spray pyrolysis, sputtering, thermal evaporation, electron beam, laser ablation, and MOCVD (Shih and Qiu, 1988; Ichikawa et al., 1988; Ginely et al., 1989; Hammond et al., 1990; Collins et al., 1991; Liu et al., 1991; Malandrino et al., 1991), but the method of choice seems to be the post deposition annealing technique. First, a precursor layer of BaCaCuO of the desired stoichiometry is sputter deposited onto a substrate. Then the film is annealed in thallium vapor which drives the thallium into the matrix forming the actual HTSC. While a one step sputter deposition is possible, the two step method consistently provides better results with average  $T_c$ 's of 125K and  $J_c$ 's typically above  $10^6$  A/cm<sup>2</sup> at 77K (Grenwald, 1991). This includes the best quality samples to date with a  $J_c$  of over  $10^7$  A/cm<sup>2</sup> at 77K (Chu et al., 1991). The two step method may also have a hidden benefit in that it isolates thallium contamination to the furnace used for the drive-in procedure.

The lattice parameters for the 2223 phase are much closer to those of the low dielectric substrates with as little as 0.75% mismatch for CeO<sub>2</sub> (Holstien et al., 1992). This means better epitaxial growth and smoother films than possible with either YBCO or bismuth (Lee et al., 1992).

Thallium-based HTSCs can be etched using the same methods as yttrium-based and bismuth-based compounds, but because of the greater stability, require less attention to reactivity and oxygen loss. The preliminary results from a wet etch process our group is currently investigating indicates that the extra strength and consistency of 2223 films makes the etching process much easier to control.

Other than the special precautions for dealing with thallium 2223 makes no special demands on packaging or characterization. Indeed, the additional strength can only serve to make these processes easier. A comparison of  $T_c$  curves for Yttrium, Bismuth and Thallium superconduc-

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tors is shown in Fig. 2.

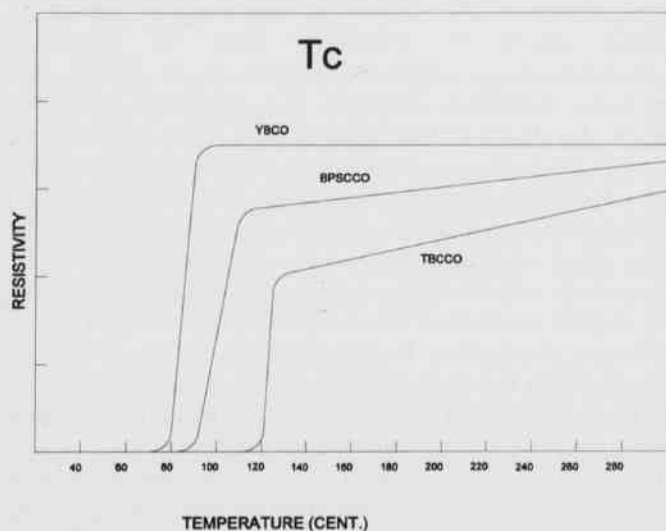


Fig. 2. Comparison of Typical  $T_c$  Curves.

### Mercury

The recent discovery of mercury based HTSCs with possible  $T_c$ s above the 145K boiling point of Freon™ is truly exciting. But, as of yet, little is known of the characteristics of the mercury-based compounds. The  $HgBa_2Ca_2Cu_3O_x$  phase (Hg 1223) with the highest  $T_c$  of 135K at ambient pressure has been shown to increase to a  $T_c$  of over 150K under hydrostatic pressure (Chu et al., 1993). However, 1223 is not produced without some amount of effort. 1223 thin films have currently been produced only by post deposition annealing under special pressure controlled conditions. With the additional cost due to current government efforts to ban the use of Freon™, the added effort necessary to produce the material and then maintain the hydrostatic pressure, means that practical Freon™-cooled HTSCs are still far in the future. Indeed, the added effort required just to achieve an additional 10K increase in  $T_c$  from thallium's 125K to 135K seems to serve no purpose, but improvements could be just over the horizon.

The reported lattice parameters combined with the initial troubles in separating out the different phases, tend to indicate that 1223 will have a  $J_c$  somewhat less than the thallium-based HTSCs (Huang et al., 1993), but this remains to be confirmed. The bottom line with mercury-based HTSCs is that we just don't know yet. A comparison of the  $J_c$ 's of the four materials is shown in table 1.

Table 1. Critical Current Density ( $J_c$ ) in A/cm<sup>2</sup>.

	YBCO	BSCCO	TBCCO	HBCCO
TYPICAL	10 <sup>4</sup>	10 <sup>4</sup>	10 <sup>6</sup>	?
MAXIMUM	1.5 x 10 <sup>6</sup>	3.4 x 10 <sup>6</sup>	2.8 x 10 <sup>7</sup>	?

### Summary and Conclusion

Yttrium base HTSCs, while having several drawbacks, have only one advantage. The comparatively low toxicity of the component materials. While, bismuth-based HTSCs have much more to offer than the yttrium based compounds, the current production of viable bismuth thin films requires the additional of lead. This tends to nullify any benefits relative to thallium-based HTSCs. Most processes used in MCM production have been demonstrated for thallium HTSVs with significantly better results than any other material. Mercury-based materials have shown some prospects and raised some new questions, but until they can be produced with more ease and characterized more definitively, they offer no apparent advantages. However, they definitely warrant more research.

While the evidence does not totally rule out any of the candidate HTSCs, the majority of the information indicates that thallium-based HTSCs should be the HTSC of choice in MCM applications.

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