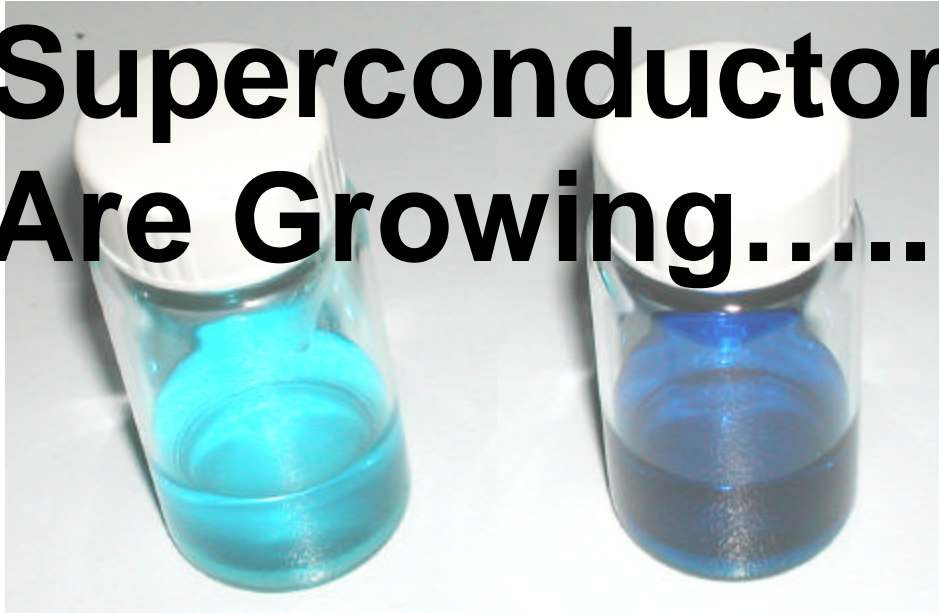


Superconductors Are Growing.....



Interest in superconducting materials around the world is on the rise. Within the laboratories at the **University of Wollongong Institute For Superconducting & Electronic Materials** one research team is developing a thin film superconductor that is grown from chemical solutions. Report by T Carolan.

The key to the future of the worlds electricity transmission and much more may be contained in the blue solutions pictured above. These are one of the first steps in the latest method being investigated for creating affordable superconducting materials. It is believed that in the future, superconducting materials will cause dramatic changes in the way electricity is transmitted and how electronic and magnetic devices operate.

What are superconductors?

High purity metals generally show a gradual decrease in electrical resistivity as temperature decreases. When temperatures come close to absolute zero (0K) the resistivity reaches a very small finite value. Some other special materials instead of exhibiting a gradual decrease show a sudden drop in resistivity down to zero

at low temperatures. These are called superconductors. The temperature at which their resistivity drops is known as the Critical Temperature, T_c .

For superconducting metals and metal alloys the T_c is between 0 and 20 K. [1] Therefore making use of the superconducting properties of these metals would require expensive operations to achieve these extremely low temperatures. These metal superconductors are considered impractical and uneconomical for this reason.

More recently it has been discovered that some ceramics also display superconducting properties. These have critical temperatures of over 90K (-183°C) and are referred to as "High Temperature Superconductors" (HTS). This is because temperatures greater than that of Liquid Nitrogen (77K) are

considered practical and economic operating temperatures compared to those requiring liquid helium or hydrogen.

It is these HTS materials that have captured the attention of researchers around the world, including those at the University of Wollongong Institute For Superconducting & Electronic Materials (ISEM). One such HTS ceramic is Yttrium Barium Copper Oxide, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (abbreviated to either YBCO or BYC). The crystal structure of this ceramic is known as perovskite. A photomicrograph of it is shown to the right (figure 1).

YBCO is a type II superconductor, which means it is completely diamagnetic in low applied magnetic fields. Diamagnetism refers to magnetic fields being excluded from the material in the superconducting state (The Meissner effect). As the applied magnetic field on a Type II superconductor is increased, the material transforms from the superconducting to normal state. During the transformation it exists in a mixed state where magnetic fields can gradually begin to penetrate the material. Over this range of critical magnetic field strength YBCO contains both superconducting and normal regions simultaneously. In contrast,

Type I superconductors do not exhibit a critical range, but have one critical field strength at which the transformation from diamagnetism occurs.

The ceramic high temperature superconductors have limitations that must be overcome if they are to become competitive with traditional conductors. Some disadvantages are their brittleness and high cost of fabrication. To make them practical, ways must be found to manufacture them into useful forms at a low cost. This is what is currently being done at UOW ISEM.



Figure 1-Photomicrograph of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, magnified 150x, to show its complex Perovskite type crystal structure. [1]

The institute, directed by Professor Shi Xue Dou, consists of more than 50 researchers and post-graduate students working on different projects [2].

Marie Roussel is a PhD research student. Her topic is the formation of superconducting thin films by chemical synthesis from solution. Researchers at MIT have previously developed this method and it is considered as

one of the potentially cost effective methods of production. In her experiments Marie uses a Strontium Titanium Oxide (SrTiO_3) single crystal substrate and a solution of YBCO (the blue solutions pictured on page 1).

One SrTiO_3 single crystal substrate sample was removed from a sealed

sample jar, carefully unwrapped from beneath several layers of paper to reveal a tiny (approximately 4mm x 4mm), flat, dark grey square, which unfortunately, to the untrained eye does not appear as impressive as may have been anticipated. The single crystals are used because grain orientation (texture) effect how the superconductor forms.

The blue solution is deposited on this substrate. It is then heated in a special furnace (figure 2) at about 400°C to allow the solution to decompose into the compound. It is then heated further (over 700°C) to anneal the sample and cause “epitaxial nucleation” of the superconductor on the substrate surface. The furnace operates with a controlled atmosphere. A typical experiment may use 20% Nitrogen gas and 20% Oxygen. Bubbling the gases through water (centre-front of figure 2) as they enter the furnace is done to increase the humidity of the furnace atmosphere to allow the correct reactions and film growth to occur.

It is only early stages for this particular PhD project and it is building on previous research. “The solution method is very sensitive to the stoichiometry of the solutions,” concedes Marie. This is one hurdle in the development of the thin films so far which she is hoping to overcome. Other variables such as the temperature of the furnace are also important factors. If it is too hot, undesired evaporation will occur and if it is too cool the necessary reactions for film nucleation and growth will not take place.



PhD student,
Marie Roussel

“The solution method is very sensitive to the stoichiometry of the solutions”

The research at this stage includes experimenting with different temperatures, annealing times, atmospheres and heating rates in the furnace to find the most successful combination to produce a good superconducting YBCO thin film.

The second stage of the research is to characterise the thin films that are produced. This involves techniques such as X-ray Diffraction and magneto-optical imaging.

X-ray Diffraction methods can be used to determine if the thin YBCO film has formed properly. If the trace from the X-rays show the intensity of the diffracted peaks from the substrate as too high and does not show peaks from the film it can indicate that the film is still amorphous or may be too thin.

Magneto-optical imaging works on the principles explained earlier of diamagnetism which excludes applied magnetic fields from the superconducting regions (Meissner phase) of the film. The MO images depict desirable dark areas, with no magnetic flux which indicates the superconducting state. The light regions show where the magnetic flux is able to penetrate the material.

Magneto-optical techniques have been employed in German research [3] for similar purposes, to determine the instability of magnetic flux in YBCO samples when using a focused laser pulse to disturb it. This results in formation of branchlike light regions where superconductivity is lost.

The aim of Marie's research is to create satisfactory films that can eventually be produced economically. She knows that, "If these films can be produced at low cost, there will be a lot of commercial interest"

In other research it has generally been found that the critical current densities of the films decrease with thickness. The aim of most research is to achieve high critical current densities in films over a micron thick because these are the ones that will become economically relevant and competitive with traditional conductors [4].

Another avenue of the superconductor research is concentrating on developing a method

"If these films can be produced at low cost, there will be a lot of commercial interest"

to manufacture coated conductor wires by using a variety of different deformation textured metal substrates with different buffers and the liquid-metal-organic deposition technique.

This is being carried out at American Superconductor and Oak Ridge National Laboratory in USA. Previously, HTS wires have been manufactured as oxide powders in tubes (OPIT) [5]. These have been put to practical applications in some trials such as transformers at power plants. They have also been used for power cables, marine propulsion motors, utility generators and magnets for materials processing [6].



Figure 2- The laboratory furnace used for heating the samples to allow the growth of YBCO thin films

It is thought that the coated conductor wires will have advantages over OPIT. Firstly, the process can allow high volume production and is potentially low cost. Also the wires and tapes should have superior mechanical properties. The manufacture of these layered composite materials involves 5 steps.

First, the substrate is hot-rolled to the required dimension, and allowed to recrystallise so that the desired texture is produced. Conducting substrates such as Ni are used. Secondly an oxide buffer is deposited on the strip. Thirdly the YBCO precursor film is deposited. This then is heated in precisely controlled conditions to cause Oxygen take-up, YBCO conversion and decomposition. The final processing step is to slit the strip into the required widths for particular applications.



Figure 3- University of Wollongong ISEM [2]

Some issues that have arisen with the development of these metal alloy substrates is that a very smooth surface must be achieved. There must also be a very uniform texture after the rolling of the substrate. Because the metals are ductile, the roughness of the substrate can be a problem.

Overall however, these techniques have been able to achieve high critical current densities over a few cm of tape (up to $106\text{A}/\text{cm}^2$) [7].

Wollongong University (pictured below) is just one of many institutes around the world that is working on YBCO. Similar experiments on the method of growing YBCO thin films from chemical solution have previously been carried out at MIT Cambridge and elsewhere, as early as 1994 [8].

Other single crystal substrates have been tried, instead of SrTiO_3 , including LaAlO_3 . Also other methods for deposition, instead of chemical synthesis have been used. For example pulsed laser deposited films and evaporative deposition. The advantage of the UOW method of chemically deriving the films is the ease of deposition over larger areas

and the ability to precisely control the overall film composition. Which means it can be produced more cheaply.

Other types of HTS

An alternate path of superconductor research is MgB_2 thin

films. These have been found to have high current densities and are superconducting below 39K. Films of MgB_2 can be fabricated by pulsed laser deposition onto Al_2O_3 substrates. [9] This research has been carried out at the university of Oslo, Norway, Russia, and Korea. It has also been found that MgB_2 magnetic flux properties show

instability even at low temperatures. This is a drawback that must be investigated before they can be put to practical use [9].

Another recently discovered High Temperature superconducting material is made of mercury, barium, copper and oxygen. This was discovered by Scientists at the Eidgenossische Technische Hochschule [10]. The possibility of this compound being used commercially is not likely due to the toxicity of the Mercury it contains. However it is promising for researchers that new HTS are still being discovered. This particular one has a Critical Temperature of 133 Kelvin.

Once good HT superconducting films are able to be synthesised, and when suitable substrates and substrate buffer materials are found, the possible applications are extensive, according to Marie Roussel, "they will be able to make wires, tapes or whatever they like" with it. The commercial applications are endless.

Acknowledgements:

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