

now be prepared in bulk form, as *E. Kaldis* (ETH Zürich) explained during his presentation. This so-called 248-phase has a T_c of 80 K. The critical current density is comparable to that in the 123-phase, but the 248-phase shows a significantly improved oxygen stability.

A number of presentations discussed the preparation and properties of Bi-Sr-Ca-Cu-O and Tl-Ba-Ca-Cu-O superconductors. In both systems two superconducting phases with $T_c > 77$ K exist. While in the Tl-system it is possible to isolate the high- T_c and low- T_c phases, this is not so in the Bi-based system. The formation of the low- T_c phase apparently proceeds much faster here than the high- T_c phase. Larger fractions of the high- T_c phase are observed after reaction times of 50 to 100 hours, while the low- T_c phase appears after only a few hours of sintering. In several presentations the stabilizing effect of Pb doping on the high- T_c phase in Bi-Sr-Ca-Cu-O was discussed. From X-ray spectra it would appear that the Pb enters the structure on the Bi sites, as *S. Amelinckx* (Univ. of Antwerp) reported. Other dopants, e.g. Nd, Sm or Gd, seem to reduce the amount of high- T_c phase in the Bi-Sr-La-Cu-O system, as shown on a poster by *M. Raveau* et al. (Univ. of Caen).

H. J. Scheel (Univ. of Geneva) summarized the activities on crystal growth of oxide superconductors. Impurities at a level as low as 0.1 wt.% interfere significantly with crystal growth, so the starting materials should be at least of 99.99% purity. Even though many groups are working on crystal growth of high- T_c superconductors, there are still no large untwinned single crystals of good quality available. One reason for this is insufficient knowledge of the phase diagrams under certain conditions, such as oxygen partial pressure, CO_2 content, etc. Even at this symposium dominated by materials scientists, a conspicuous lack of phase equilibria studies was apparent.

While the current carrying capability in sintered bulk high- T_c superconductors remains a problem because of small coherence lengths, anisotropy and granularity (*R. Flükiger*, Kernforschungszentrum Karlsruhe), the situation with thin film superconductors looks more promising. A large number of groups presented papers on the prepara-

tion and characterization of high- T_c superconducting thin films. A wide variety of methods, such as sputtering, thermal- and laser-evaporation, molecular beam epitaxy, etc., were employed to produce superconducting films, and a general distinction was made between in-situ processing and post-anneal processing. In-situ processing takes place in the presence of activated oxygen at relatively high pressures during deposition. Post-anneal processing requires additional oxygen annealing to crystallize the films following deposition. The primary advantage of in-situ processing over post-anneal processing, in addition to the fact that no additional oxygen annealing is necessary, is the lower substrate temperature (500 to 700°C as compared to 800 to 900°C, respectively), which helps to avoid film-substrate reactions. A further problem with films made by post-anneal processing is their high surface roughness which makes electronic applications of these films difficult or impossible (*A. Kapitulnik*, Stanford Univ.). An interesting approach was presented by *H.-U. Habermeier* (Max-Planck-Institut für Festkörperforschung, Stuttgart). He exposed his films to an oxygen plasma during deposition as an alternative to furnace annealing and showed it to be an excellent tool to restore the oxygen content of the films, even at temperatures as low as 300°C. The most commonly used substrates were single crystalline SrTiO_3 and MgO , but also films deposited on yttria-stabilized zirconia, Al_2O_3 , sapphire, LiNbO_3 , and Si were discussed. In view of potential applications, in particular applications in connection with semiconductor devices, these substrates are of primary interest.

In conclusion, there were no sensational reports, and no spectacular new T_c records were announced; the fax machine in the conference office certainly did not run hot as it did at the Interlaken meeting at the beginning of the year. However, this does not mean that no progress was made in the field of high- T_c superconductors, only that the hectic phase of the research and development disappeared—at least for the time being. The dust of previous stampedes towards higher T_c has settled to make room for serious, systematic work towards a more complete understanding of these novel materials.

... and Colorado Springs

After the conference on Critical Currents in High- T_c Superconductors held in Snowmass Village in August of last year, Colorado was, once again, the site of a major superconductivity conference. This time it was the Conference on the Science and Technology of Thin Film Superconductors that took place on November 14–18, 1988 in Colorado Springs, Colorado, USA. Over 200 scientists and engineers from around the world attended this conference, which was

organized by the U. S. Department of Energy (DOE), the Solar Energy Research Institute (SERI), the National Institute of Standards and Technology (NIST) (formerly National Bureau of Standards, NBS), The Naval Research Laboratory (NRL), and the Lawrence Berkeley Laboratory (LBL). Thirty-six invited and contributed papers, and more than 40 posters were presented on thin film deposition techniques, characterization, theory, device design and ap-

plications as well as bulk material studies related to thin films. In addition to the technical presentations, a set of short courses was offered during the first day of the conference to bring the audience up to date with current research in the area. The courses, organized by Lawrence Berkeley Laboratory's Superconductivity Research Center for Thin Film Applications, were given by such prominent scientists as *S. Wolf* (NRL), *J. R. Kwo* (AT&T Bell Labs.), *J. Clarke* (UC Berkeley), and others. The topics ranged from an introduction to superconductivity, through fabrication and characterization of superconducting thin films, to superconducting electronics applications. These short courses were quite a success, since they offered the scientists involved in the preparation of films some insight into the problems engineers encounter when designing devices based on these films.

The technical presentations started off with representatives of DOE, NRL, and NIST giving overviews of the activities at their respective government agencies. Especially impressive was the budget increase for basic energy science at the DOE from \$ 12.4 million in the fiscal year 1987 to \$ 36.7 million in 1989.

Presentations during the first two days of the conference focused on film preparation and characterization. Among methods commonly used to deposit superconducting films were thermal and electron beam co-evaporation, laser ablation, dc- and magnetron sputtering, including multitarget sputtering, molecular beam epitaxy (MBE), metalorganic chemical vapor deposition, etc. A much discussed preparation technique was the laser ablation or laser enhanced deposition technique. A pulsed excimer laser beam is directed on a target mounted in a vacuum chamber under the heated substrate. The emitted atoms or molecules from the target collect on the substrate and form the film. Laser fluxes in the range of 0.1 to 5 J cm⁻² were reported. The advantage of this method is quite obvious: a relatively simple arrangement is sufficient to produce films of 0.1 μm thickness in only a few minutes. The not very uniform coverage of the substrate by this method is an inherent problem which could be overcome, e.g. by a scanning set-up or a similar technique. A post-deposit oxygen annealing step can be avoided by plasma-assisted laser deposition, as *H. S. Kwok* (State Univ. of New York (SUNY), Buffalo) reported. The plasma between target and substrate is produced by a low pressure dc oxygen discharge. In addition to being a "one-step" process, this method is compatible with semiconductor processing since substrate temperatures as low as 400°C are sufficient. *J. R. Kwo* (AT&T Bell Labs.) used her MBE apparatus with a reactive oxygen species excited by a microwave plasma contained in a flow tube reactor. In this case, the substrate temperature was 550°C. *R. H. Hammond* (Stanford Univ.) also used a microwave cavity to produce atomic oxygen during film deposition. Using an oxygen partial pressure versus temperature diagram determined by *R. Bormann* (Univ. of Göttingen), he compared the film deposition and

cooling conditions which he used with the data published by other groups.

Preparation of superconducting thin films made by a new method, electron beam flash evaporation, was discussed during the short courses as well as in several talks and posters. As with the laser ablation method, the flash evaporation process convinces by its simple approach. Small pellets (approx. 0.2–0.5 g) of the oxide components are evaporated to completion by a high-intensity electron beam from a water cooled copper hearth. It takes 30 to 40 s to completely evaporate a 0.3 g pellet, as reported by *P. R. Broussard* (NRL), and depending on the experimental set-up, the evaporation of one pellet results in a film thickness contribution of about 20 nm according to the information on the poster of *M. F. Davis* et al. (Univ. of Houston). No deposition-rate measuring schemes and complex feed-back circuits are required for this method. The stoichiometry of the films is very close to that of the pellet, even when large substrates are coated. The method has been used successfully for the preparation of both YBa₂Cu₃O_x and Bi₂Sr₂CaCu₂O_y superconducting films. Best results were obtained with Bi-based films deposited on MgO substrates, showing zero resistance critical temperatures of 85 K after short post-deposition annealing at 865°C in oxygen. Reproducibility of the films varies considerably among the different groups and the methods employed. Very reproducible films, however, resulted from the so-called "BaF₂ process", first used by *P. M. Mankiewich* (AT&T Bell Labs.). In this process, metallic Y and Cu together with BaF₂ are co-deposited in the presence of oxygen. The films are amorphous and insulating. Post-deposition annealing in wet oxygen is required to convert the films into superconductors with critical temperatures near 90 K. Even though post-deposition annealing is necessary to obtain superconductive films, these films are highly reproducible and are very robust and generally withstand the rough treatments with water and solvents during lift-off lithography. Many researchers reported on efforts to produce films by a one-step or in-situ process, i.e. a deposition procedure not requiring post-deposition oxygen annealing to produce a superconducting film. Common to all reported procedures are the relatively low substrate temperatures of 500 to 700°C as compared to conventional multi-step processing requiring post-deposition annealing at 800 to 900°C. A development towards lower deposition temperatures is of course favorable in view of electronic applications that might require common processing steps for superconductors and semiconductors.

Throughout the entire meeting the issue of the determination of the substrate temperature came up repeatedly. The substrate temperature is one of the most crucial deposition parameters for all film preparation methods, yet in many cases not very accurate statements as to the real substrate temperature could be made, since many experimenters measure the temperature of the heating block rather than that of the substrate itself. According to one study,

however, there can be a temperature difference of as much as 30 K between heater block and substrate surface, which led *R. H. Hammond* to conclude that the thermal contact between heater and substrate is of extreme importance.

Substrate materials commonly used in the preparation of superconducting films were SrTiO_3 , MgO , cubic ZrO_2 (YSZ), and sapphire, all dielectric materials. Single crystalline SrTiO_3 , which has only a 0.5% lattice mismatch with $\text{YBa}_2\text{Cu}_3\text{O}_7$, is the preferred substrate for achieving epitaxial films exhibiting the highest critical current density measured to date (of order 10^6 A cm^{-2} in zero field at 77 K). Because of their high dielectric losses, neither SrTiO_3 nor MgO is a suitable substrate material for microwave applications. Here the recently discovered LaGaO_3 and LaAlO_3 provide excellent microwave properties (low dielectric constant, low loss tangent) and are easier and less expensive to produce than SrTiO_3 . Structure and lattice constants are favorable for growing epitaxial films of perovskite related superconductors. *R. W. Simon* (TRW) showed dielectric measurements confirming the desirable microwave properties of LaAlO_3 substrates. He speculated that BaZrO_3 might also turn out to be a good substrate material; an indication thereof could be the successful use of ZrO_2 buffer layers used on some $\text{YBa}_2\text{Cu}_3\text{O}_7$ films. *Simon* encouraged researchers to focus on new substrate materials; there is "no reason to be married to SrTiO_3 ", as he put it, "since this material has nothing to offer except high prices and bad high frequency properties". *H. S. Kwok* described films made by plasma-assisted laser deposition on dielectric, semiconducting, and metallic substrates. Especially interesting were his critical current measurements of films deposited on stainless steel. J_c of these flexible films decreased by as much as 20% from an initial value of about 1000 A cm^{-2} by repeated bending. *J. Tate* (Technische Universität München) showed that the films deposited by thermal co-evaporation on Si substrates had a 100 Å amorphous SiO_2 layer between substrate and $\text{YBa}_2\text{Cu}_3\text{O}_7$ film. The motivation for depositing films on semiconducting substrates was, of course, with a view to potential electronics applications, but the Munich group also argued that "if you can make films on Si, you can make them on anything".

The critical current density of superconducting films, apart from T_c the single most important parameter for any application, was most often measured by the four-point method. *S. Wolf* emphasized the need for a uniform standard in determining the critical current density. The ASTM standard of $1 \mu\text{V cm}^{-1}$ now used in many publications was really designed for long wires. As a better standard for short samples, the $\rho < 10^{-11} \Omega \text{ cm}$ specific resistivity criterion was suggested. The even more stringent criterion of $\rho < 10^{-14} \Omega \text{ cm}$ is being used by the Fermilab for their magnet wire. Since in many cases the critical current density is measured by less stringent criteria due to small samples and insufficient measurement resolution, it is important for comparison to include the measurement criterion along with the value of the critical current density.

Talks presented during the third day of the conference centered around Josephson junctions as well as electronics and microwave applications of thin film superconductors. *J. Przybysz* (Westinghouse R&D Center, Pittsburgh) gave an excellent overview of his group's effort to build Josephson shift registers. These and other digital elements are required for high speed signal processing, e.g. in microwave electronics, radar technology etc. There are essentially two ways to obtain superconducting digital circuits. One approach consists of using persistent current loops that are coupled to shift a single bit to the next loop; the other approach is first building logic gates from Josephson switches and then assembling shift registers and other circuits with these gates. The fastest Josephson shift register to date is a Fujitsu one-bit shift register operating at 2.3 GHz—still slower than the current state of the art GaAs technology. However, the Josephson shift register has the potential to reach 60 to 100 GHz clock frequencies, much higher than can be hoped for with GaAs circuits. One drawback with Josephson electronics is that in many cases the semiconductor-based measuring equipment stops working well before the limit of the former is reached.

R. Koch (IBM, Yorktown Heights) showed recent developments on SQUIDS made by magnetron sputtering Tl-Ba-Ca-Cu-O films on cubic zirconia and SrTiO_3 substrates, followed by annealing and patterning by photolithography. In addition he reported on voltage noise power measurements in thin film stripes. He showed that voltage noise power does not follow a square law, as would be expected for resistive noise, but varies almost linearly with the voltage. Such a behavior suggests that the noise is created by the motion of thermally excited flux vortices across the sample. Among other applications discussed were photo-detectors for visible and infrared wavelengths, superconducting transmission lines for analog signal processing, voltage standards and an analog-to-digital converter based on a high-speed superconducting counter.

Interesting thoughts on the benefits of using the proximity effect with high- T_c superconductors were presented by *V. Z. Kresin* (LBL). A combination of an A15 superconductor with a high- T_c superconductor would effectively raise T_c of the A15 material. This combination could be useful in utilizing the good current carrying capabilities of metallic superconductors at higher temperatures. The T_c in the high- T_c superconductor of such a combination is lowered by the same token; but that can be useful in some cases, e.g. measuring normal state properties at low temperatures as done in fermiology. There is no experimental evidence for the proximity effect in high- T_c superconductors since very good quality films are required for these studies.

The last conference day was devoted to the "Colorado Superconductivity Shootout", an opportunity to compare thallium versus bismuth versus yttrium superconducting compounds. The basis for the "shootout" was a series of talks given by six speakers who then formed a panel to lead the subsequent discussion. The best aspects of

Tl-superconductors were presented by the inventor himself, *A. M. Hermann* (Univ. of Arkansas, Fayetteville). He pointed out the high current density in both bulk and thin films of Tl-based superconductors, as well as their excellent thermal and chemical stability. Bi-superconductors were defended by *R. J. Soulen* (NRL) and *N. G. Dhere* (SERI). Finally, *R. Simon* (TRW) presented a line-up of the three classes of high- T_c superconductors together with Nb as the representative for the conventional superconductors, much in the style of Consumer Report Charts on VCRs or automobiles. Although each material has advantages in specific areas, there were no overall winners or losers. The common consensus was that more effort is necessary to tame and understand these materials more thoroughly before selecting the superior superconductor.

During the following panel discussion, the toxicity of Tl-compounds was a prominent topic. *D. S. Ginley* (Sandia National Laboratories) stressed, as he had done during his talk on Tl-films earlier in the conference, that Tl is not exceptionally toxic. The problem is not the toxicity but the question of how to handle the substances. Tl, which accumulates in soft tissues, has a half-life of 20 to 30 days in the body; however BaCO_3 , which is about 100 times less toxic than Tl, accumulates in bone marrow and thus re-

mains inside the body considerably longer than Tl. The toxicity of Tl is quite well documented in a Johnson & Matthey summary sheet that includes data on skin absorption, lethal doses, etc.

The Conference on the Science and Technology of Thin Film Superconductors was in fact an exciting and important meeting, just as the organizers promised in their announcement. As a result of the very specialized focus on thin film superconductors, the number of attendees was manageable and it was not necessary to organize concurrent sessions, certainly a point that increased the efficiency of this meeting. The conference provided an excellent opportunity to meet researchers from industry as well as national laboratories and academic institutions, and to discuss a wide spectrum of problems ranging from preparation techniques through methods of characterization to circuit design using superconducting switching elements. In today's over-abundance of superconductivity conferences, this conference was well worth attending.

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