

A Low-Cost Approach to Fabrication of Multinary Compounds for Energy-Related Applications

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R.N. Bhattacharya and S.K. Deb

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A Low-Cost Approach to Fabrication of Multinary Compounds for Energy-Related Applications

Raghu N. BHATTACHARYA and Satyen K. DEB

National Renewable Energy Laboratory
1617 Cole Boulevard, Golden, CO 80401

Non-vacuum electrodeposition and electroless deposition techniques with a potential to prepare large-area uniform precursor films using low-cost source materials and low-cost capital equipment are very attractive for the growth of compound materials for superconductors and photovoltaic applications. In the first part, a low-cost electrodeposition (ED) method will be discussed for fabrication of high-temperature Tl-oxide-based superconductors. In the second part, electrodeposition and electroless deposition of semiconductor Cu-In-Ga-Se thin films will be discussed.

KEYWORDS: low-cost fabrication; multinary compounds; electrodeposition, electroless deposition; superconductors; photovoltaics

Non-vacuum electrodeposition and electroless deposition techniques with a potential to prepare large-area uniform precursor films using low-cost source materials and low-cost capital equipment are very attractive for the growth of compound materials for superconductors and photovoltaic applications.

In the first part of the paper, a low-cost electrodeposition (ED) method will be discussed for fabricating high-temperature Tl-oxide-based superconductors. The primary technical challenge that must be satisfied to permit high-temperature superconductor (HTS) wire or tape in superconducting magnets or power-related applications is the successful demonstration of a low-cost, high-field, high-current-carrying wire or tape with acceptable mechanical properties ($>10^5$ A/cm² at 77 K in magnetic fields of >0.2 T). The Tl-based superconducting oxides are excellent candidates because of their high transition temperatures reaching to 127 K and unique features in their growth morphology. Research on the single-layer Tl-1223 compound, with Pb, Bi, and Sr substitution for the Tl and Ba, respectively, has recently received more attention due to the promise of improved transport behavior in magnetic field and phase stability competitive with the YBa₂Cu₃O_x (YBCO) compound at 77 K operating temperature.^{1,2} Electrodeposited (Tl,Bi)-(Sr,Ba)-Ca-Cu-Ag (TBSBCCO) thick-film wire or tape has considerable practical potential for fabricating a low-cost, high-field, high-current-carrying conductor suitable for superconducting magnets or power-

related applications. A multi-cation thick coating of 1-5 μ m can be electrodeposited easily at the desired stoichiometry from an electrolyte solution onto a conducting substrate. At present, we are optimizing a low-cost, commercially scalable ED processing to demonstrate biaxially textured Tl-1223 with Bi and Sr substitution on single-crystal substrates that will be transitioned to the flexible textured Ni.³ The single-crystal results will establish a base-line reference and proof of principle for transition to a suitably buffered metallic substrate. The electrodeposited superconductor precursor films were obtained by co-electrodeposition of the constituent metals using nitrate salts dissolved in dimethyl sulfoxide (DMSO) solvent. The electrodeposition was performed in a closed-cell configuration at 24°C. A number of electrodeposition runs were performed with different electrolyte compositions, and the precursor films were analyzed by inductively coupled plasma (ICP) spectrometry to establish the stoichiometry of the deposited elements. The cation ratios of the electrodeposition bath were adjusted systematically to obtain (TlBi)_{0.9}Sr_{1.6}Ba_{0.4}Ca₂Cu₃Ag_{0.2} (TBSBCCO-Ag) precursor compositions. A typical electrolyte bath composition for the TBSBCCO-Ag films consisted of 0.018 M TlNO₃, 0.009 M Bi(NO₃)₃·5H₂O, 0.297 M Sr(NO₃)₂, 0.212 M Cu(NO₃)₂·6H₂O, and 0.002 M AgNO₃ dissolved in dimethyl sulfoxide solvent. The films were electroplated by using constant potential at -3 V. Pole-figure measurements of electrodeposited (TBSBCCO) films, with thicknesses between 1-5 μ m, clearly show strong biaxial texturing. The rocking curve and phi scan of TBSBCCO on 300-Å Ag/LaAlO₃ show a full-width half-maximum (FWHM) of only 0.52° and 0.5°, respectively, consistent with a very high-quality film. Transport measurements for the ED films show critical current density J_c values above 10^6 A/cm² at 77 K in zero magnetic field (Fig.1). The criterion for the critical current density (J_c) measurements was 1 μ V/cm electric field. The magnetic field was applied parallel to the c plane of the superconductor (H//c). The J_c value of ED Tl-1223 films are comparable to the highest value ever reported for any processing technique, including pulsed-laser deposition, sputtering, and e-beam techniques.⁴⁻⁶

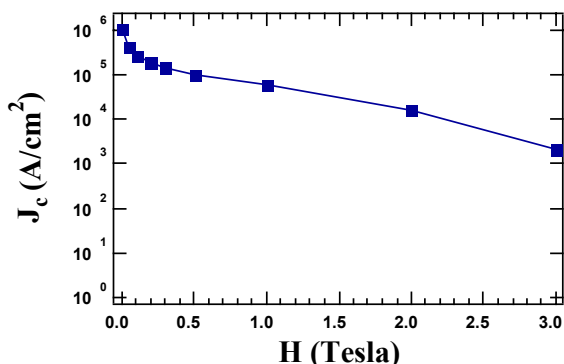


Fig. 1. The magnetic-field dependence of transports J_c at 77 K (H//c) of an ED-TBSBCCO-Ag film on LAO

In the second part of the paper, electrodeposition and electroless deposition of semiconductor Cu-In-Ga-Se thin films are discussed. Thin-film $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS)-based solar cells have the highest performance efficiencies in both small-area devices and large-area (4000 cm^2) modules: 18.8%⁷ and 12.1%,⁸ respectively. Test modules and arrays based on CIGS-based devices have been operating outdoors for more than 10 years with little degradation.⁹ The 18.8%-efficient device prepared in our research laboratory⁷ is based on a multistep process using physical vapor deposition (PVD). The PVD technique is challenging to scale up because of film non-uniformity and low material utilization. Sputtering techniques are suitable for large-area deposition; however, they require expensive vacuum equipment and sputtering targets. Therefore, non-

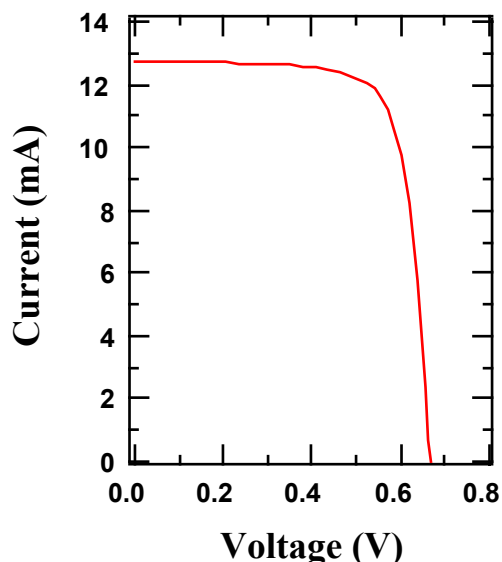


Fig. 2. I-V characteristics of an ED device ($V_{oc} = 0.666 \text{ V}$, $I_{sc} = 12.76 \text{ mA}$, $J_{sc} = 30.51 \text{ mA/cm}^2$ Fill Factor = 75.56%, Efficiency = 15.4%).

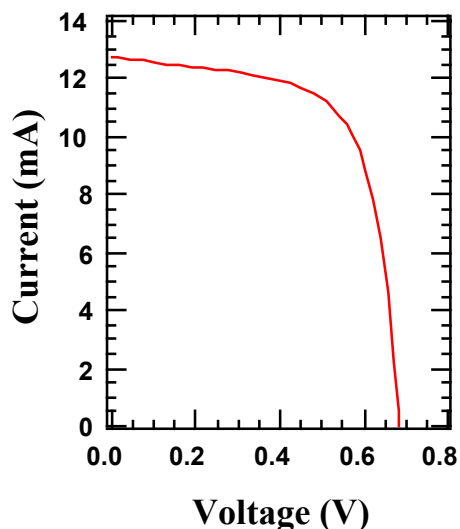


Fig. 3. I-V characteristics of an EL device ($V_{oc} = 0.6866 \text{ V}$, $I_{sc} = 12.72 \text{ mA}$, $J_{sc} = 29.29 \text{ mA/cm}^2$, Fill Factor = 66.87%, Efficiency = 13.4%).

vacuum electrodeposition and electroless deposition (EL) techniques^{10,11} with a potential to prepare large-area uniform precursor films using low-cost source materials and low-cost capital equipment are very attractive for the growth of CIGS layers for photovoltaic applications. We have fabricated 15.4%-efficient (Fig.2) and 13.4%-efficient (Fig.3)

$\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS)-based devices from electrodeposited and electroless-deposited precursors. As-deposited precursors are Cu-rich films and polycrystalline or amorphous in nature. Additional In, Ga, and Se were added to the precursor films by physical evaporation to adjust the final composition to $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$. Addition of In and Ga and also selenization at high temperature are crucial to obtain high-efficiency devices. The films/devices have been characterized by ICP spectrometry, Auger electron spectroscopy, X-ray diffraction, electron-probe microanalysis, current-voltage (I-V) characteristics, and spectral response.

The ED and EL deposition processes are simple and fast, and they can synthesize multi-component precursors for subsequent processing into high-quality multinary compounds for energy-related applications.

REFERENCES

- [1] R.N. Bhattacharya, R.D. Blaugher, A. Natarajan, C.M. Carlson, P.A. Parilla, D.S. Ginley, M. Paranthaman, A. Goyal, and D.M. Kroeger, *Jour. of Superconductivity*, **11**, 173 (1998).
- [2] T.J. Doi, T. Yuasa, T. Ozawa, and K. Higashiyama, *Jpn. J. Appl. Phys.*, **33**, 5692 (1994).
- [3] A. Goyal, D.P. Norton, J.D. Budai, M. Paranthaman, E.D. Specht, D.M. Kroeger, D.K. Christen, Q. He, B. Saffian, F.A. List, D.F. Lee, P.M. Martin, C.E. Klabunde, E. Hartfield, and V.K. Sikka, *Appl. Phys. Lett.*, **69**, 1795 (1996).
- [4] W.Y. Lee, V. Y. Lee, J. Salem, T.C. Huang, R. Savoy, D.C. Bullock, and S.S.P. Parkin, *Appl. Phys. Lett.*, **53**, 329 (1988).
- [5] Z.F. Ren, C.A. Wang, and J.H. Wang, *Appl. Phys. Lett.*, **65**, 237 (1994).
- [6] R.S. Liu, D.N. Zheng, J.W. Loram, K.A. Mirza, A.M. Campbell, and P.P. Edwards, *Appl. Phys. Lett.*, **60**, 1021 (1992).
- [7] M.A. Contreras, B. Egaas, K. Ramanathan, J. Hiltner, A. Swartzlander, F. Hasoon, and R. Noufi, *Progress in Photovoltaics*, July, (1999).
- [8] F.H. Karg, 11th International Photovoltaic Science and Engineering Conference (PVSEC 11), September 20-24, Sapporo City, Hokkaido, Japan, (1999).
- [9] H.S. Ullal, K. Zweibel, and B. von Roedern, *Proc. 26th IEEE PVSC*, Anaheim, CA, 301 (1997).
- [10] R.N. Bhattacharya, W. Batchelor, J.F. Hiltner, and J.R. Sites, *Applied Physics Letters*, **75**, No. 10, September, (1999).
- [11] R.N. Bhattacharya, W. Batchelor, H. Wiesner, F. Hasoon, J.E. Granata, K. Ramanathan, J. Alleman, J. Keane, A. Mason, R.J. Matson, and R.N. Noufi, *J. Electrochem. Soc.*, **145**, 3435 (1998).

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