

Film Fabrication Technologies at NREL

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ABSTRACT

The National Renewable Energy Laboratory (NREL) has extensive capabilities for fabricating a variety of high-technology films. Much of the in-house work in NREL's large photovoltaics (PV) program involves the fabrication of multiple thin-film semiconducting layers constituting a thin-film PV device. NREL's smaller program in superconductivity focuses on the fabrication of superconducting films on long, flexible-tape substrates. This paper focuses on four of NREL's in-house research groups and their film fabrication techniques, developed for a variety of elements, alloys, and compounds to be deposited on a variety of substrates. As is the case for many national laboratories, NREL's technology transfer efforts are focusing on Cooperative Research and Development Agreements (CRADAs) between NREL researchers and private industry researchers. The reader is encouraged to consider and explore the application of these film-fabrication technologies for their own needs by contacting the author or the principal scientists at NREL, referenced below.

INTRODUCTION

Chemical deposition and physical deposition are the two principal classifications for a multitude of film-fabrication technologies, whether the films are thin (about 1 micron thick or less) or not (thicker than 1 micron). Among the chemical deposition technologies used by NREL researchers are several chemical vapor deposition techniques, liquid phase epitaxy, solution growth, and several electrochemical techniques. Among the physical deposition technologies are several sputtering techniques, physical vapor deposition using electron beams or resistance heating, molecular beam epitaxy, and melt coating. These techniques or their variations have been used at NREL to deposit a variety of metals, compounds, and alloys as amorphous, polycrystalline, or crystalline films. Among the critical factors in identifying an appropriate deposition technology are the control precision needed for the amounts of the elements used in the films—especially important in the case of semiconducting compounds and their dopants—the effect of the deposition technology on the crystallinity of the final films, and the deposition rate—an especially important parameter for production costing.

A historical description of NREL's film fabrication technologies and the materials deposited is in reference 1. The deposition techniques at NREL include electron beam evaporation, physical vapor deposition, magnetron (DC and RF) sputtering, ion-beam sputtering, electrodeposition of multielement compounds, molecular beam epitaxy, liquid-phase epitaxy, electrolytic plating, electroless deposition, plasma-enhanced chemical vapor deposition, photochemical vapor deposition, hot-wire catalytic deposition, melt sheet growth, and melt coating. Several of these techniques, or their variations, have been used to deposit films of Si, amorphous Si, amorphous Ge, amorphous C, Au, Sn, Zn, Ag, Mo, W, GaAs, GaAlAs, GaInP₂, GaAsP, InP, GaP, CuInSe₂, CdS, In₂O₃(Sn), SnO₂(Sb), ZnO(Al), Ta₂O₅, TiO₂, MgF₂, ZnS, MoO₃, WO₃, diamond-like carbon films, YBaCuO compounds, BiSrCaCuO compounds, TlBaCaCuO compounds, other refractory metals, other metal oxides, silicon alloys, and amorphous-silicon alloys.

NREL also has a long history of substantial funding (50% of NREL PV funds) for industrial research in photovoltaics; and much of that research is devoted to manufacturing processes, including film fabrication research for thin-film devices. Subcontract research to industry is a legitimate technology transfer activity at NREL, although industry itself is supported to develop technology, and no "transfer" takes place.

This paper will highlight four of NREL's film fabrication technologies and their achievements within NREL's PV and superconductivity programs. Three are chemical deposition technologies that have proven to be advantageous for the controlled deposition of multielement compounds and alloys. The fourth is a physical deposition technology with known advantages for use in production. NREL's in-house research capabilities are available to US PV companies, superconductivity companies, and other companies interested in film-fabrication technologies.

METALORGANIC CHEMICAL VAPOR DEPOSITION

J. Olson and coworkers successfully fabricated record-high-efficiency photovoltaic devices using a custom-built metalorganic chemical-vapor-deposition system (2, 3). They grew their epitaxial layers of GaInP₂ and GaAs in an atmospheric-pressure MOCVD vertical reactor, and achieved efficiencies for the conversion of sunlight to electricity as high as 29% (active area), a record for this technology. The system was built with a standard run-vent configuration. The Ga, In, P, As, and Zn sources were compounds of trimethylgallium, trimethylindium, phosphine, arsine, and diethylzinc. Carbon doping came from a CCl₄ source consisting of reagent-grade CCl₄ housed in a conventional bubbler, with Pd-diffused H₂ used as the carrier gas. Growth was done on zinc-doped GaAs single-crystal substrates.

During their work on improving device performance, this group developed an in-situ growth-rate measurement technique using diffuse reflectance normal to the growth surface. The technique allows for measurement of real-time surface roughness, in addition to growth rate. The period of interference fringes obtained from the diffuse reflectance was compared with cross sections measured by a scanning-electron microscope and shown to be inversely proportional to the growth rate.

HOT-WIRE CHEMICAL VAPOR DEPOSITION

R. S. Crandall and coworkers developed a different chemical vapor deposition technique for amorphous silicon (4). Called hot-wire-assisted chemical vapor deposition (HWCVD), it appears to be capable of producing hydrogenated amorphous silicon with properties superior to those fabricated by the more conventional plasma-enhanced chemical vapor deposition (PECVD). The HWCVD films are deposited using a hot filament temperature of approximately 1,900°C, to dissociate the silane gas, and a chamber pressure low enough to minimize gas collisions before the film precursors hit the substrate. The amorphous silicon films are fabricated using a SiH₄ gas flow rate of 20 sccm and either glass or silicon substrates held at varying temperatures between 40°C and 450°C. Deposition rates tended to be as much as four times faster than PECVD rates; rapid deposition rates are critical to the cost effectiveness of production technologies. Figure 1 is a schematic of this process.

ELECTRODEPOSITION

Instead of chemical vapors, R. Noufi, R. Bhattacharya, and coworkers developed an electrodeposition technique using chemical solutions for depositing superconducting films (5). Electrodeposition is an electrochemical process where materials (e.g., metals or oxides) in the proper stoichiometry are deposited on conducting substrates from chemical solutions containing the ions of interest (e.g., Cu²⁺, Y³⁺, Ba²⁺, in the case of one of the high-temperature superconductors). As is almost always the case for electrodeposition, one of the two phases contributing to an interface of interest will be a liquid electrolyte, which is merely a phase through which charge is carried by the movement of ions. The second phase at the boundary is a solid electrode (the substrate in this case), which is the phase through which charge is carried by electron movement. In general, when the potential of an electrode is moved from its equilibrium value toward negative potentials, the substance that will be reduced first ($\text{Cu}^{2+} + 2e^- = \text{Cu}^0$) is the one with the least negative redox potential. For example, in a solution containing Cu²⁺, Y³⁺, and Ba²⁺, the Cu²⁺ is reduced first, followed by the reduction of Y³⁺ as the potential of the electrode is made more negative. All three ions can be deposited on the surface of the electrode when the potential is negative enough. The relative concentrations of the constituents in the deposited films are empirically determined by the concentrations of the ions in the solution.

There are other families of superconducting compounds involving Ba, Sr, Ca, Cu, O and Tl, Ba, Ca, Cu, O (6). NREL researchers have successfully electrodeposited these compounds in their appropriate stoichiometries. A significantly high rate of fabrication, of the order of microns per minute, makes electrodeposition a likely candidate for large-scale, cost-effective manufacturing of superconducting wires or tapes. Figure 2 is a schematic of this process for the fabrication of superconducting tapes made from thallium compounds.

PILOT LINE SPUTTERING

Many PV researchers have concluded that sputtering does too much damage to films during fabrication to yield the optimum electronic properties needed for high-efficiency photovoltaic devices. Yet T. Coutts and coworkers adapted this deposition technology, with known production advantages to a high-quality solar-cell design destined for space applications (7). Using Ar sputtering gas, InP solar cells were fabricated using two sputter guns and depositing successive layers of indium-tin-oxide (ITO). The first thin layer provided a shallow homojunction in the InP substrate, while the second provides part of an antireflection coating needed for high performance of the completed solar cell. Additional layers, patterned electrical contacts, and a post-deposition heat treatment provide controlled changes in the electrical and optical properties of the solar cell and complete the processing of the final cell. Thirty-two solar cells, each 4 cm² in area, were completed in the pilot production. The histogram of efficiencies ranged from about 15% to over 16%. The project demonstrated that the sputtering process can be used for these relatively-large-area devices and that the highest efficiency, 16.2%, is comparable to the highest reported from another production method. Further, the process can be configured for in-line production rather than batch production, characteristic of many CVD production processes.

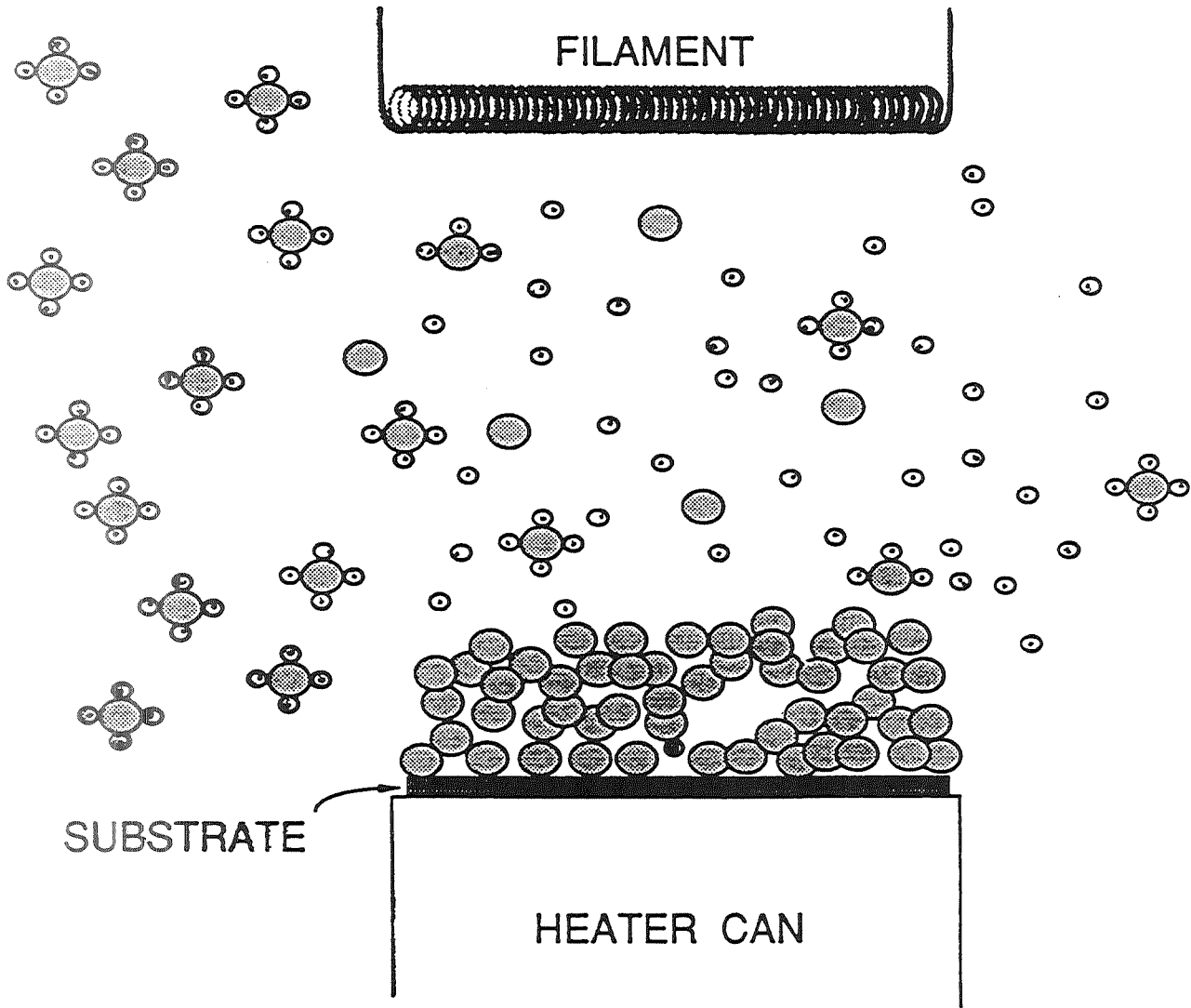
CONCLUSION

This paper has briefly described four film fabrication technologies developed by NREL researchers for either multilayer PV devices or high temperature superconducting coatings. Each of the research groups mentioned above has achieved distinction within its respective research community through the development of these particular film-fabrication processes for high-efficiency PV devices or superconducting coatings. For U.S. PV companies, superconductivity companies, or other companies interested in high-technology films and coatings, these and other NREL research groups are resources available through formal cooperative R&D agreements, such as CRADAs.

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FIGURE 1. HOT-WIRE CHEMICAL VAPOR DEPOSITION



| | | | |
|---|---------------------------------|---|------------------------|
|  | SILANE (SiH₄) |  | SiH₃ |
|  | HYDROGEN |  | SILICON |

Deposition Rate $\approx 10 \text{ \AA/second}$

TI Tape Scaleup Scenario

FIGURE 2.

