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LLNL Vapor Phase Manufacturing Progress Report June through December 1995

T. Anklam, J. Benterou, L. Berzins, D. Braun, C. Haynam, G. Heestand, and M. McClelland

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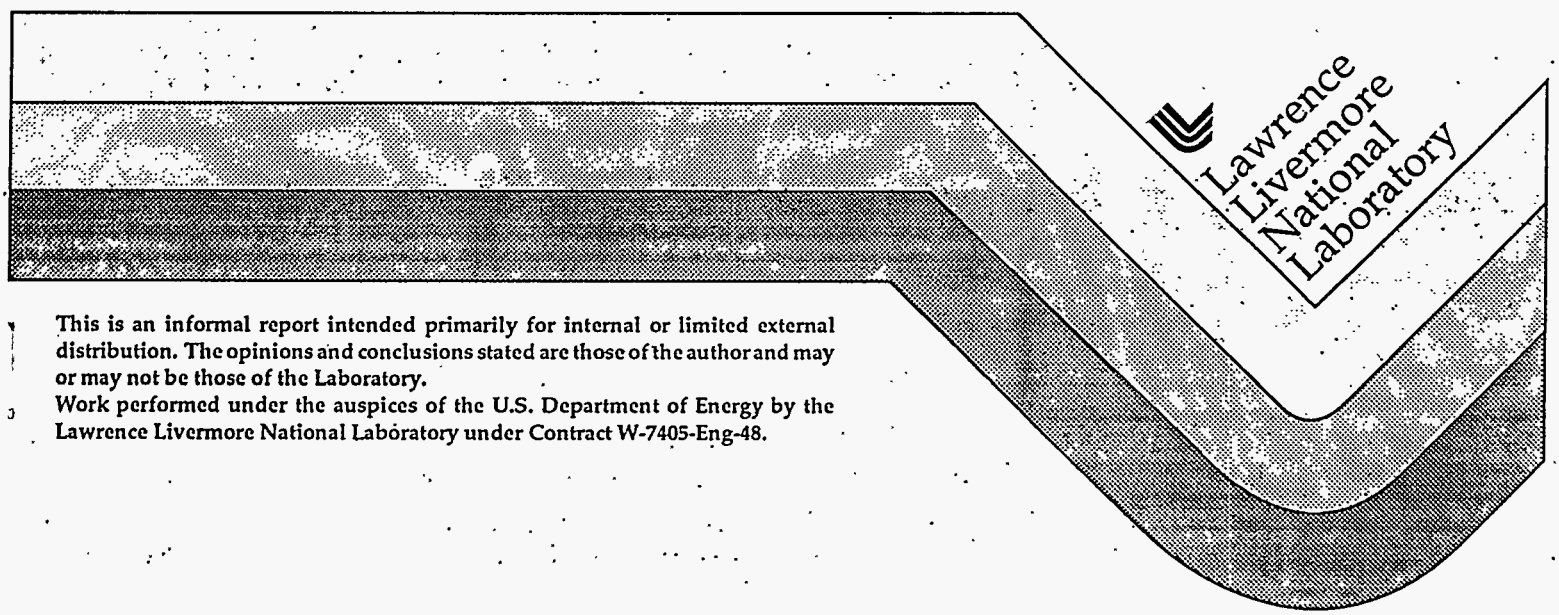


LLNL Vapor Phase Manufacturing
Progress Report
June through December 1995

Tom Anklam, Jerry Benterou, Leon Berzins, Dave Braun, Chris Haynam, Glenn Heestand, Matt McClelland

Introduction

This report documents progress and status of the LLNL's Vapor Phase Manufacturing Project. LLNL received ARPA funding on May 25, 1995. Listed below are the LLNL milestones for Project Year 1 (June 1995 to May 1996) as taken from LLNL's proposal to ARPA [1]:

1. **Demonstrate titanium and niobium monitoring at 3M site.**
2. **Demonstrate aluminum monitoring at LLNL.**
3. **Complete baseline melt and vapor plume model for the metal matrix process.**
4. **Prototype a laser at LLNL to monitor Cu.**
5. **ZrO_2 monitoring demonstration at LLNL.**
6. **Selenium monitoring demonstration.**

Our scope of work includes support for each of the four different consortia in the ARPA Vapor Phase Manufacturing Program:

Project	Milestones	LLNL Project Leader
Metal Matrix Coatings*	1,2,3	Tom Anklam
Thin Film Photovoltaics	4,6	Tom Anklam
Advanced Thermal Barrier Coatings	5	Glenn Heestand
Thin Film Superconductors	4	Tom Anklam

*Model Factory Program

Significant progress has been made toward achieving all of the above milestones and is reported below.

Demonstrate Titanium and Niobium Monitoring at 3M Site

LLNL Project Members: Leon Berzins, Shirley Galanti, Mike Potter, Jerry Benterou, Jeff Cooke, Tom Anklam

Consortium Contact: Jonathan Storer, 3M

New Focus Project Engineer: Mike Bortz

Our work to date has focused on titanium monitoring. This reflects 3M's priority to develop a reliable sensor that can be used to demonstrate controlled evaporation of Ti-6Al-4V (titanium, 6 wt% aluminum, 4 wt% vanadium) in their research coater in St. Paul, and then to quickly transition the sensor technology into their West Virginia factory. Work on niobium has been deferred until the sensor for titanium is well in hand.

There are four elements to the titanium sensor system: the laser light source, optical transport and signal detection hardware, physical interface of sensor to coating chamber and software to analyze laser absorption data and turn it into a measurement of titanium evaporation rate. New Focus Lasers, Inc. has primary responsibility for the development of the light source, LLNL has responsibility for establishing the specification for the laser and is responsible for the other three elements of the sensor system.

LLNL has previously demonstrated laser absorption spectroscopy based vapor sensors for a variety of materials: uranium, gadolinium and iron to name a few. Recently, Stanford has reported controlled evaporation of yttrium using an FM spectroscopy based vapor monitor[2]. However, the titanium sensor requires a blue, tunable diode laser light source. The technical approach is to frequency double red light from an external cavity diode laser with a periodically polled $LiNbO_3$ doubling crystal. This is highly developmental. New Focus has been collaborating with the Stanford Center for Materials Research to develop a doubling crystal suitable for titanium monitoring.

New Focus has delivered a first prototype laser that operates at the specified titanium wavelength (391.5 nm). This laser produces 10 to 20 μW of optical power. In contrast, the red diode lasers used to monitor uranium, etc. deliver about 1 mW of optical power. The low blue power level has necessitated redesign of the uranium monitor optical transport and signal detection hardware and the physical interface of the sensor to coating chamber.

All optical components, lenses, mirrors, fiber optic cable, acousto-optic modulator, and fiber collimators, were reviewed and modified as needed for improved performance at 391.5 nm. Leaded glass was removed from the window assembly on the vacuum vessel because it strongly absorbs UV light. However, the leaded glass is also a very effective X-ray shield. Removal of the leaded glass required incorporation of metal shielding boxes around the sending and receiving units. Labyrinth seals are used on all seams to assure an X-ray tight interface.

The third modification to the system was acquiring more efficient receiving and reference detectors. This was done in collaboration with New Focus. Preliminary tests at LLNL indicated that the New Focus' photo detector was up to an order of magnitude more efficient than the detection system previously in use at LLNL. The down side was that the detectors utilized very small area photo diodes. This configuration was sensitive to the spatial mode of the light as well as beam movement. To address these concerns the detector was modified and now uses a large area photo diode.

While the redesign effort has greatly reduced the sensor system optical power requirements, sensor performance at these power levels is marginal. New Focus and Stanford are evaluating improved methods to fabricate $LiNbO_3$ crystals that should ultimately yield high optical power levels.

LLNL has also evaluated an alternate doubling crystal (KTP). The KTP crystals produced roughly 50 μw power and seemed less prone to degradation with operating time. However, the KTP crystals are not yet available at the most desirable titanium wavelength. The project is currently pursuing both the improved $LiNbO_3$ and KTP options. While we expect steady improvements in optical power levels, this will likely be a performance limiter for the sensor system for at least the next year.

Despite difficulties due to low power, we have integrated the New Focus blue laser with the LLNL optical transport and signal processing system and demonstrated on-line monitoring of titanium evaporation. The demonstration was performed at LLNL in October. Jonathan Storer from 3M, Milton Chang, President of New Focus and Michael Bortz, New Focus' Project Engineer were present during the demonstration.

Titanium was evaporated in a 15 kW Temescal electron beam evaporator. At 15 kW, the Ti density is too low to monitor the 391.5 nm transition (the 3M system operates at 90 kW). Instead, we tuned the laser to a nearby transition that is about an order of magnitude stronger (392.1 nm). Discrete optics were used to deliver light to the evaporator rather than optical fibers. This improves transport efficiency, but is less robust than fiber delivery. Figure 1 is the titanium optical depth as a function of frequency as measured by the sensor. Figure 2 is the titanium atom number density as a function of time during the evaporation run. The Temescal vaporizer evaporates a fixed charge of material so the run duration was only a few minutes in duration. However, the test was sufficient to confirm the basic operability of much of the integrated sensor system.

The software used to generate Figure 2 was developed at LLNL. Copyrights to the software is held by the United States Enrichment Corporation (USEC). To facilitate the research phase of this project, USEC has made this software available for use in the monitoring demonstration at 3M.

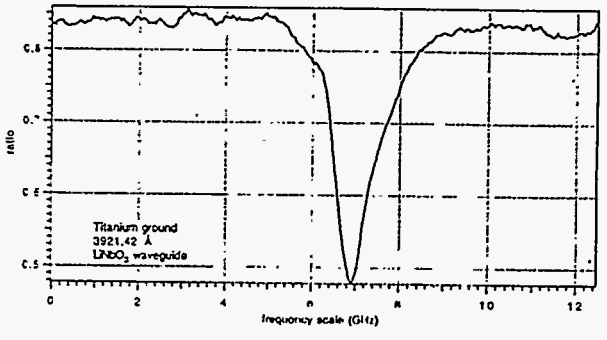


Figure 1. Titanium optical depth vs. frequency as measured by vapor monitoring system.

New Focus has procured all of the hardware needed to assemble a titanium sensor system at 3M and most of the hardware has been received. Our plan is assemble the complete system at LLNL, including fiber delivery, and perform a complete system checkout on a multi-hundred kilowatt evaporator system. Optical path lengths and titanium vapor densities will be similar to those expected in the 3M system. We will pay particular attention to assuring that all chamber interface hardware is X-ray tight (X-ray fluxes in the vacuum chamber are on the order of 10^9 R/hr).

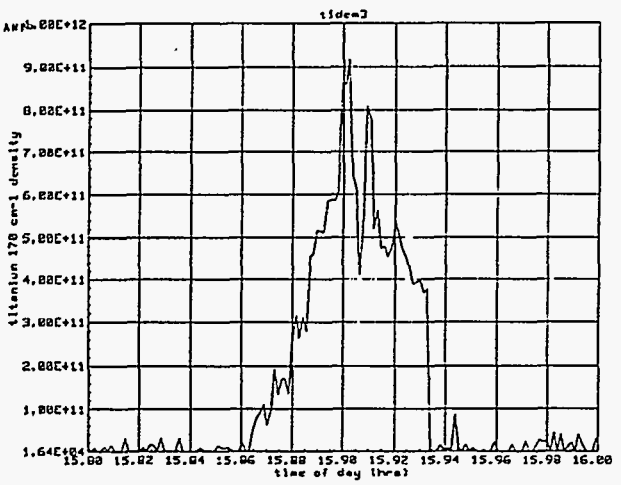


Figure 2. Titanium ground state density as measured by vapor monitoring system.

Our goal is to have the sensor system in place at 3M by early February.

Demonstrate Aluminum Monitoring At LLNL

LLNL Project Members: Chris Haynam, Jerry Benterou

Consortium Contact: Jonathan Storer, 3M

Aluminum has relatively few spectral lines that can be accessed with frequency doubled diode laser technology, and those lines that can be reached are extremely strong. For high throughput coating applications, aluminum is essentially opaque to the transmission of resonant light. This problem is not unique to aluminum. Copper and indium are both strong absorbers. To address this limitation, LLNL has been developing a new sensing technique that does not rely on resonant absorption spectroscopy.

The new technique, referred to as group-velocity delay based vapor monitoring, relies on the fact that the index of refraction is a strong function of frequency near resonant absorption lines. A laser can be detuned from line center to reduce absorption, but the light still undergoes a measurable phase shift that is a function of the detuning and the vapor density.

Light from a diode laser is injected into a Bragg cell where it is split into a fundamental beam and one which is frequency shifted by 200 MHz. The two beams are optically combined and sent through the vapor plume. Because the two beams are at different frequencies, they experience a different phase shift. This phase shift is linearly related to the vapor density. The phase differential between the beams is measured by a vector voltmeter. This method was first developed by LLNL to measure high opacity vapors of calcium and strontium [3].

Our challenge is to take what is basically a spectroscopy laboratory technique and adapt it to real time process monitoring. Figure 3 is a block diagram of the development prototype system. The development system utilizes a frequency doubled Ti-Sapphire laser rather than a diode source. A diode source will be integrated into the sensor system in Project Year 2.

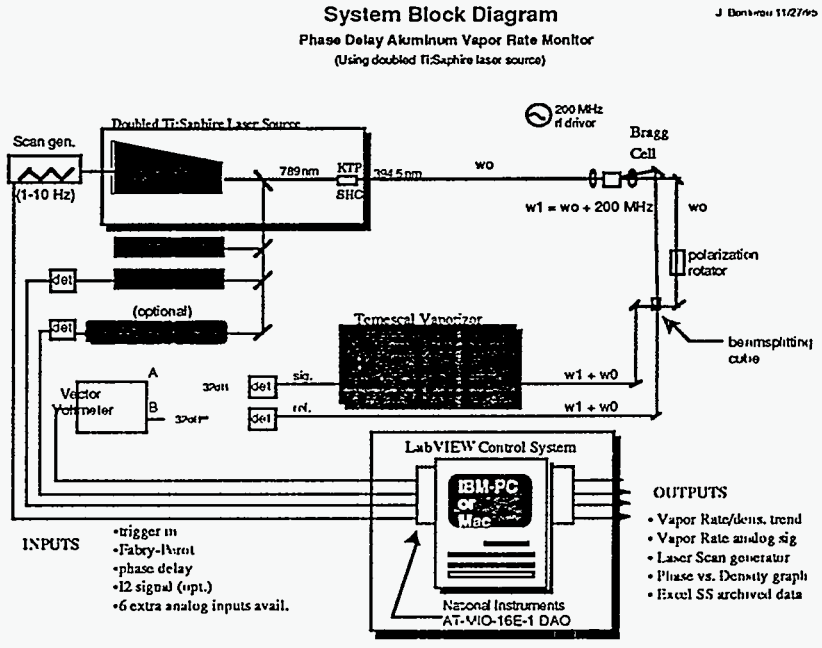


Figure 3. Prototype group velocity delay vapor monitor.

Key technical issues are generation and detection of low power ultraviolet laser light and developing appropriate software for integrating sensor calibration, data processing and laser control functions. In Project Year 1, the diagnostic laser will be an internal cavity frequency doubled Ti-sapphire laser. The light from this laser will be Bragg shifted, recombined on a beam splitter, and fiber optically delivered to the vaporization chamber. The low light levels are particularly difficult to handle due to the necessity of high-bandwidth detection of the 200 MHz beat signal between the fundamental and shifted lasers. Both PIN diodes and photo multiplier tubes are sensitive and fast enough to investigate as candidates.

Software development will be done in two steps. In the first step, a simple Labview program will monitor the phase delay of a fixed frequency laser. Since the phase delay depends on the square of the frequency difference between the laser and the atomic resonance, the program will also monitor and control the frequency offset of the laser. This method requires use of a commercially available wavelength measurement device with a resolution of 50MHz. This wavelength measurement device will be eliminated in the second step of software development. The advanced software will scan the laser and measure, in real time, the center of the transition using symmetry properties of the phase delay signal. This will both remove an expensive component and increase the accuracy and reproducibility of the density measurement.

Progress has been made on all aspects of this project. A Ti-sapphire laser has been set up in the frequency doubling mode in the appropriate area to support both initial tests on the 15 kW Temescal e-beam vaporizer and in our high rate ETF chamber. Photo multipliers have been ordered, received, and tested and appear to be appropriate detectors. With higher gain detectors, background light from the chamber and room lighting becomes an issue. Bandpass filters to block out stray light have been ordered and various light baffling techniques are being investigated.

Shakedown testing of the system was completed in November. A simulated aluminum vapor test was performed in the lab. A heated iodine vapor cell served as a surrogate Al vapor source. The optical layout was similar to that in Figure 3 except that the laser source was a ring dye laser operating at 570 nm and the Al vapor source was replaced by the I_2 cell. A heterodyne beat frequency of 200 Mhz was observed on both the reference and signal detectors. The amplified detector outputs were connected to a vector voltmeter. The output of the vector voltmeter was recorded on an X-Y plotter as the laser frequency was scanned through an I_2 absorption line.

The software should be ready for testing in January. The initial setup of lasers, detectors, electronics, and software will be tested in the Temescal chamber in early January and then used in the high rate ETF system in February.

The group-velocity delay based vapor monitor has applications beyond vapors which have only strongly absorbing resonant lines. Absorption spectroscopy based vapor monitors require a careful match between the strength of the absorption line and the process vapor density. If the line is too strong the diagnostic saturates, if too weak the diagnostic has excessive noise. Once an appropriate absorption line is found, a diode laser must be found that can tune to that line. These constraints tend to make each sensor system highly customized to an application.

The group-velocity delay technique expands the range of absorption lines that can be used to monitor a particular element. This increases the likelihood that a common sensor system can be used for monitoring a number of different elements. For example, the wavelength range around 390 nm is very rich in spectral lines for a wide range of metals: Ti, Al, Mo, Fe, Ta, V, Zr, Co, Gd. If strongly absorbing lines can be used, then a common laser and sensor system might be used for any of these elements.

Routine application of group-velocity delay based vapor monitors is probably several years away. Until then, absorption and possibly FM spectroscopy (for low vapor density applications) based systems will be the workhorse for process monitoring in production environments.

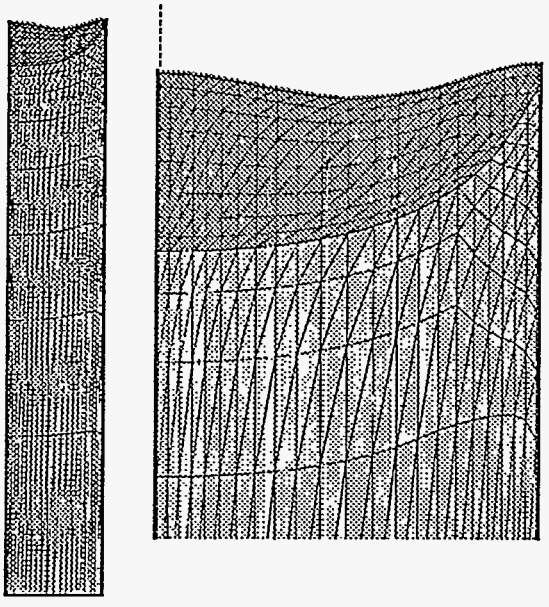
Complete Baseline Melt and Vapor Plume Model for the Metal Matrix Process

LLNL Project Members: Matt McClelland, Dave Braun, Tom Meier, Rick Palmer, Greg Hawkins, Leon Berzins

Consortium Contact: Jonathan Storer, 3M

The objectives of this task are to develop physically based models of the vaporization and vapor transport phenomena in the 3M fiber coating process. Ultimately, these models along with the sensors described above, will form the basis for an intelligent control system for the metal matrix process. These models are also critical to design of a scaleable coating system for the high temperature superconducting film process.

LLNL, in collaboration with the University of Washington, developed a powerful finite element methodology for the modeling of electron beam evaporation as a part of its work on uranium evaporation. This approach, incorporated in the MELT computer code, is currently being adapted to model 3M's titanium alloy evaporators. A unique deformable mesh strategy is used to explicitly calculate the locations of the upper and lower pool boundaries coupled with fluid flow and energy transport (see Figure 4).



1.1.3.1095.2422pb01

Figure 4. Finite element meshes deform along vertical spines to track two interfaces.

An initial model has been formulated and we are beginning to analyze evaporation experiments that have been run at 3M. Figures 5 and 6 show results for Ti6Al4V evaporation with uniform and ring beam profiles. Note the vapor thrust depression in the pool free surface caused by the ring beam. Free surface deformation is coupled to fluid flow and energy transport in the pool. Deformation effects dampen the sensitivity of vaporization rate to changes in beam power and other variables. Models which don't include these effects tend to over predict improvements in vaporization rate gained by increasing electron beam power.

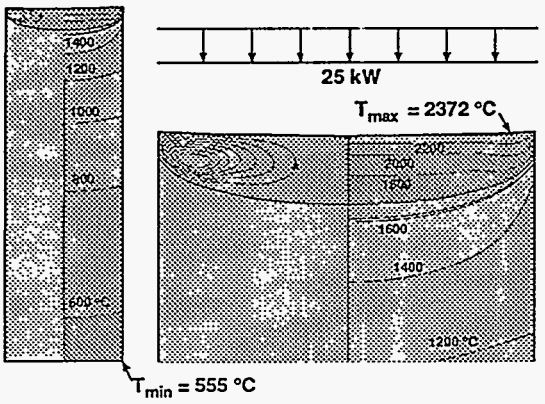


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Figure 5. Velocity and temperature fields for the uniform e-beam profile with power = 25 kW.

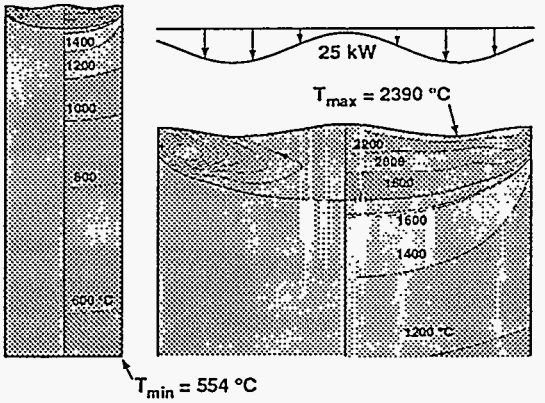

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Figure 6. Velocity and temperature fields for the "ring" e-beam profile with power = 25 kW.

At the end of the first year we expect to complete a careful comparison of MELT predictions with results from 3M and LLNL experiments (described below). This comparison of evaporation rates, heat flows, and pool cross-sections will provide the basis for improvement in the model parameters and assumptions.

In a parallel effort, we will develop a separate boundary-layer model for multi-component species transport and evaporation at the top surface of the melt pool. For volatile species, the diffusional resistance to transport at the top surface strongly influences evaporation rates. The input bulk flow and temperature fields will be calculated using MELT.

In the area of vapor transport, we are collaborating with 3M to adapt the DMCS (Direct Monte Carlo Simulation) code to the modeling of electron beam evaporated vapor plumes. Monte Carlo methods allow a computation to follow vapor from the high density continuum zone near the vapor source to the rarified hypersonic flow zone near the deposition surface. By its nature, DSMC codes can easily track the concentrations of the individual elements in a multi-species vapor plumes. Our objective is to develop a physically based model which can predict the spatial distribution of vapor density and composition as a function of vapor source operating conditions and the power profile of the electron beam footprint. 3M is extremely interested in this capability because it will assist them in improving the capture efficiency of the metal matrix coating process.

For multiple source evaporators, our objective is to accurately calculate inhomogeneities in vapor composition that result from incomplete mixing of the plumes from the different vapor sources. The Monte Carlo method allows explicit calculation of collisional effects that inhibit plume mixing. This capability is of interest to 3M for the evaporation of intermetallic compounds. It is also of interest to the high temperature superconducting film consortium for the design of a scaleable coating system for YBCO.

A two dimensional model of an axi-symmetric vapor plume has been developed. It has been benchmarked against the case of a radially expanding vapor with no angular density dependence (i.e. density is only a function of radius). For this simple case analytic solutions for the vapor density and temperature as a function of radius are known, and the results of the DSMC simulations are in close agreement with those solutions.

Simulations modeling nozzle sources have shown a slight dependence of the resulting spatial density profile on the area of the nozzle. Smaller nozzles produce slightly broader profiles. These simulations have also shown that the results are not greatly effected by changes in the atomic collision cross-section. This is fortunate since their values are not well known.

Multi-species simulations have also been performed in which the diffusion of the lighter species on the density gradients inside the plume have been studied. According to classical collision theory the diffusion coefficient of a species is proportional to $1/\sqrt{m}$. The DSMC simulations show that as expected the lighter

species migrate preferentially to the edges, but that the resulting concentration variations in the main portion of the plume are small (<10% relative).

The code is currently being adapted to handle a spatially varying particle source of multiple species. This will be used to simulate vaporization from the hot liquid under the beam footprint, as well as the cooler surrounding pool. Due to its large surface area, the pool is an important source for vaporizing the more volatile elements of an alloy due to its large surface area. The temperature profiles from the melt model simulations will be used to set the spatially varying vapor source strengths of the various species.

Along with model development, we are preparing for a series of titanium alloy evaporation experiments which are specifically designed to support model development and validation. We are currently installing a bottom fed crucible in the LLNL vaporizer. This will allow us to more closely approximate the 3M evaporation process. Fiber optics connect the vaporizer to a large diagnostic laser lab. This will allow very detailed real time assessment of vaporizer performance as a function of operating conditions. Shakedown testing of the bottom fed crucible are planned for January. The first set of Ti6Al4V co-vaporization tests are planned for March of '96.

Prototype a Laser at LLNL to Monitor Cu

LLNL Project Members: Chris Haynam, Bill Molander, Gaylen Erbert, Jerry Benterou

Consortium Contact: Bob Hammond, Stanford University

Copper evaporation monitoring is even more challenging than aluminum. Copper is a strong absorber like aluminum, thus it requires a group-velocity delay based vapor monitor. The longest wavelength transition in copper is 325 nm, $LiNbO_3$ and KTP are too absorbing at 325 nm to allow the use of periodically polled doubling crystals. The objective of this task is to develop a laser light source capable of accessing the 325 nm copper transition.

The technical approach is to use external cavity doubling of light from a 650 nm diode laser. Light from the fundamental diode enters an external cavity containing a lithium triborate doubling crystal. The cavity produces a high circulating fundamental power. Doubling efficiency increases as the square of the fundamental laser power density, so the high circulating power is needed to get adequate power at 325 nm.

There are a number of technical challenges to overcome. First, the cavity must be frequency locked to the fundamental laser as the laser is scanned over the copper absorption line. Our approach is to use a polarization locking technique which was successfully used by a group at JPL. Second the cavity needed for this application is very compact. The doubling crystal's length and size as well as the optic's focal lengths have been optimized for doubling efficiency, and their size requires fabrication of special mounts. Finally, the short wavelength light is difficult to transport by fibers to the coating chamber. We have transmitted light at this wavelength through about 50 meters of fiber for use in diagnostics in the past. Starting with a few milliwatts of power, the attenuation was not a problem. We plan to measure attenuation in fibers at 325 nm to quantify system power requirements. An industrial version of our diagnostic will employ a diode operating at between 50 and 100 mW with a cavity conversion efficiency exceeding 1% giving up to 1 mW of output power. At these power levels and shorter fibers (less than 10 meters) required for commercial installations similar to those currently envisioned for Ti, fiber attenuation should not be a limiting problem.

The optical cavity design has been completed, the optics ordered, and most have been received. We are currently working on designing the optical mounts. Following the design, the mounts will be fabricated, the cavity assembled, and initial conversion efficiency measurements made. Shortly after this demonstration, the cavity lock loop will be developed and wavelength scanning initiated.

ZrO_2 Monitoring Demonstration at LLNL

LLNL Project Members. Glenn Heestand, Chris Haynam, Tom Meier. Rick Palmer, Greg Hawkins

Consortium Contact: Mike McLaughlin, General Electric - CRD

To date we have completed two high power ZrO_2 vaporization runs at LLNL. The first run was our first attempt at high power vaporization of ZrO_2. Lasers were not present in our first run

because we wanted to get experience in vaporizing ZrO_2. Since we do not yet have a bottom feed capability, we cut one of GE's ZrO_2 cylindrical feed ingots in half, so we would have a flat surface, and laid this in the crucible on top of some molybdenum plates. The system was brought up to 45 kW over a 45 minutes time period to the point where we had a clear liquid pool and were doing significant vaporization as evidenced by the drop in pool level. We had significant outgassing but we were able to work through it and gained confidence in our ability to vaporize ZrO_2.

Based on our success during the first run we did a second run with lasers. Lasers were tuned to near 15374 cm^{-1} where Q band absorption was clearly seen. At our highest power level (54 kW) we saw close to 20% absorption for a transition out of the J = 20 state (Figure 7). This is very encouraging and tells us we have enough signal to work with and should get some meaningful information. Since commercial ZrO_2 vaporizers are operated at higher power levels we expect to see even higher absorption levels. Our ETF facility has over a 200 kW power capability.

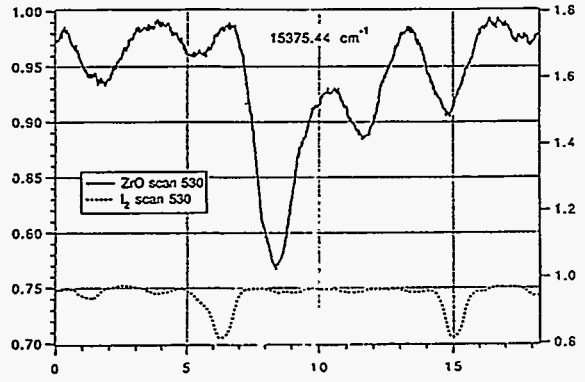

Figure 7. Absorption spectra of ZrO near 15375.44 cm^{-1} (6504A).

Upon completion of the installation of the bottom load feeder in January we will no longer be limited in run duration and will be able to obtain considerably more data in a given run. After January data will be taken which will enable the laser absorption diagnostic to be a valuable tool in the development and control of the vaporization process used to produce thermal barrier coatings. Early data taken during our first two vaporization runs has given us confidence that we will be successful in our thermal barrier coating project.

Selenium Monitoring Demonstration

LLNL Project Members: Tom Anklam, Mark Havstad, Leon Berzins, Chris Haynam

Consortium Contact: Robert Wendt, ITN

This task is in support of the thin film photovoltaics coating process.

In November, LLNL staff visited ITN to refine our scope of work. Lockheed Martin - Denver was also represented at the meeting. We discussed at length possible diagnostic approaches for the photovoltaic deposition process. Based on those discussions, we are recommending a revision to our plan.

A laser based diagnostic for selenium control appears less well suited for this application than for the applications discussed above. Selenium does not evaporate atomically. Instead it tends to form a molecular vapor, Se_n. The value of n is not well known, there is undoubtedly a range of cluster sizes in the plume and this distribution probably varies with evaporation rate. Each cluster configuration has its own unique spectroscopy so interpretation of a laser absorption signal is complex.

ITN's highest priority is to have a means to make a real-time measurement of the quality of the CIS layer. This will initially be used to develop a model for CIS layer performance as a function of layer deposition conditions. Eventually, it will become the basis for an intelligent control system. Real time reflectometry or ellipsometry appears well suited to this need.

Ellipsometry relies on the fact that reflection and transmission of polarized light is different for light which is polarized parallel to the plane of incidence and that which is polarized perpendicular to the plane of incidence. For example, if linearly polarized light, containing both parallel and perpendicular components, reflects off of a dielectric coating, both the phase and amplitude of the two components are differentially altered. The result is that the reflected light is elliptically polarized. An ellipsometer measures this change in polarization state and uses this information to determine the optical properties of the film and, in some cases, the film thickness. Film optical properties tend to be closely related to other film properties: stoichiometry, band gap in semiconductors, etc.

Recent publications show a growing interest in the use of ellipsometry for process control[4,5]. We are aware of a group in Germany that has been exploring the use of ellipsometry as a process control for high speed web coating applications.

Lockheed-Martin will send LLNL a series of CIS samples with known processing histories. LLNL will characterize the samples with multi-wavelength ellipsometry. In particular we will try to relate band gap to processing conditions. Our goal is to draw correlations between ellipsometry data and CIS film quality. Beyond simply evaluating the quality of the film we will attempt to correlate specific quality defects with variations in process conditions.

Once these correlations have been developed, we will then move toward developing a practical ellipsometry system for in-situ monitoring and process control. This work is complementary to another project we have underway to develop an in-situ ellipsometry system for laser ablation coating.

Process Scale-up Study for YBCO

LLNL Project Members: Tom Anklam, Dave Braun, Leon Berzins, Matt McClelland

Consortium Contact: Bob Hammond, Stanford University

This is a modeling activity in support of the thin film, high Tc superconductor project. It is not directly tied to a specific project milestone.

For the YBCO PVD process to become commercially viable, a vapor deposition process that is scaleable to high throughput needs to be developed. Hammond has proposed a large array of small electron beam vapor sources similar to those used in the semiconductor manufacturing industry[6]. A large number of atomic absorption laser probes traverse the multicomponent vapor plume, and tomography is used to reduce the data from the probes into signals that are used to control the vapor sources.

Figure 8 shows an alternate high throughput concept that is based on technology developed for the vacuum web coating industry. Three electron beam vapor sources are used to evaporate the three metallic components of the film. Atomic oxygen is bled into the coating chamber to grow the YBCO film on a moving web. Typical web and vapor source widths are on the order of 1m. The required evaporation rates are low enough so that the plume mixing is essentially collisionless. An aperture restricts the portion of the mixed vapor plume that deposits on the web and limits the range of vapor compositions that reach the web. A multi-wavelength, laser based sensor is used to monitor vapor composition and control the relative evaporation rates of the three vapor sources.

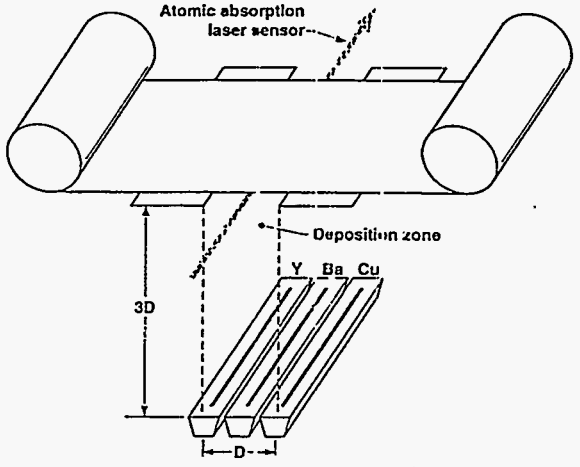

Figure 8. Proposed geometry using three individual e-beam heated sources.

Figure 9 shows the range of compositions for different aperture lengths; D is the distance between the outermost vapor sources (Figure 8). The web standoff is 3D. Note that the Ba vapor composition in the center of the aperture is slightly lower than the ideal concentration of 33%. This is to assure that the vapor does not become Ba rich at the edge of the aperture. Ba rich deposits have been correlated with poor superconducting performance. Vapor utilization, fraction of evaporated material that deposits on the web, as a function of aperture size is summarized in Figure 10. All of the cases examined have relatively low vapor utilization. However, the cost of feedstock is low, so vapor utilization can be sacrificed in order to achieve correct film composition[6].

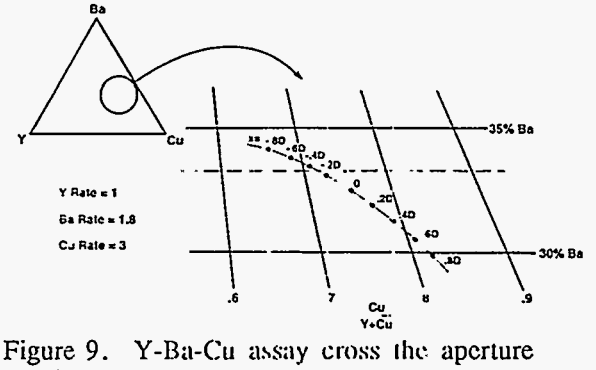

Figure 9. Y-Ba-Cu assay cross the aperture opening.

Limits of Aperture Opening	Aperture Width	Vapor Utilization		
		Y	Ba	Cu
-.2D .2D	.4D	.093	.099	.093
-.2D .4D	.6D	.143	.148	.143
-.4D .4D	.8D	.185	.197	.185

Figure 10. Vapor utilization of the proposed geometry as a function of aperture width.

Web standoff 1.5m
Deposition length 30 cm
Deposition rate 100Å/s YBCO
Web width 1m
Source length 1m
YBCO thickness 1μm

$$\text{Web speed} = V_w = \frac{\text{deposition length}}{\text{required deposition time}} = \frac{.3\text{m}}{\left(\frac{10^{-6}\text{m}}{10^{-8}\text{ m/s}}\right)} = 3.0 \times 10^{-3}\text{ m/s}$$

$$\text{Km 1m wide web/yr} = \frac{(3.0 \times 10^{-3}\text{ m/s})\,(3.15 \times 10^{7}\text{ s/yr})}{10^{3}\text{ m/km}} = 94.6\text{ km/yr}$$

Kilometers of 1cm wide = 94.6 km/yr x 100 = 9460 km/yr Tape/yr

Small plant throughput of 6000 km/yr is achieved with a 63% plant duty factor

Figure 11. Single coating chamber meets small plant throughput requirements.

Figure 11 shows that a single coating chamber meets the throughput requirement for the small production plant described in Hammond's paper[6]. The composition range and vapor utilization for this case study correspond to a 0.4D aperture width. Figure 12 shows the calculated evaporation rates for each the components. These evaporation rates should be easily achievable with electron beam evaporation.

Deposition Rates		Densities	Mass Rates	Evaporation Rates
YBCO	100Å/s	6.57 gm/cm³	71 gms/hr	
Y	20.2	4.46	9.7 gms/hr	68 gms/hr
Ba	77.4	3.50	29.3 gms/hr	198 gms/hr
Cu	21.1	8.96	20.4 gms/hr	143 gms/hr

Annual Feed Consumption

Y 596 kgs x 0.63 (duty factor) = 376 kgs

Ba 1734 kgs x 0.63 = 1092 kgs

Cu 1253 kgs x 0.63 = 789 kgs

Figure 12. Required evaporation rates for the proposed geometry.

This simple analysis shows that this process concept deserves further evaluation. Process architecture is simple and is easily scaleable to high throughput rates. Much of the base technology has already been demonstrated in the vacuum web coating industry. Important issues which are yet to be examined are the interaction of the metal vapor plume with the oxygen background gas and the level of precision required in the temporal control of the vapor sources.

References

1. T.M. Anklam and G.M. Heestand, Intelligent Processing of Materials for Vapor Phase Manufacturing - Proposed Development Plan for Vapor Physics Models and Real Time Vapor Monitors, UCRL-PROP-L-19001-1, February 1, 1995.

2. W. Wong, et al., (1995) Appl. Phys. Lett. 67: 1375-1377.

3. J.K. Crane, et al., Measurement of the Cross Sections for Collisional Broadening of the Intercombination Transitions in Calcium and Strontium, Phys. Rev. A, Vol. 49, #3, March 1994.

4. S. Kim, et al., Optical Characterization of Continuous Compositional Gradients in Thin Films by Real Time Spectroscopic Ellipsometry, Applied Physics Letters, November 13, 1995.

5. J. Koh, et al., Real Time Spectroscopic Ellipsometry Study of Hydrogenated Amorphous Silicon P-I-N Solar Cells - Characterization of Microstructural Evolution and Optical Gaps, Applied Physics Letters, October 30, 1995.

6. R.H. Hammond, Thick Film YBCO for Wires and Tapes: Scale-Up Issues and Cost Estimates, Proceedings of ISS' 95, Hamamatsu, Japan, November 21, 1995.

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