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# Evaporation Rate and Composition Monitoring of Electron Beam PVD Processes\*\*

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## Abstract

Lawrence Livermore National Laboratory (LLNL) is developing sensor and control technology to improve the quality and range of applicability of electron beam PVD. The approach being developed uses tunable lasers to measure the density and composition of the vapor plume. This paper reviews the principles of operation of laser based sensors and discusses data from experiments in which titanium and niobium are co-vaporized. Laser data agreed well with deposited film compositions and spatial variations in deposited film cross sections. Laser based vapor monitoring appears to have broad applicability and has the potential to extend the use of high rate electron beam PVD.

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## 1.0 Background

A primary limit to the full exploitation of electron beam PVD is difficulty in controlling evaporation rate and, for alloy coatings, vapor composition. A rule of thumb is that control of vapor composition is difficult for alloys with constituents differing in vapor pressure by more than about 100x[1]. This greatly limits the applicability of electron beam PVD and forces the use of lower throughput coating methods such as sputtering.

In low evaporation rate applications a variety of techniques are available for monitoring deposition rate and vapor composition. Thin film crystal monitors are common in semiconductor manufacturing and electron impact fluorescence devices and hollow cathode lamp based spectroscopy can provide both density and composition information. However, in high rate vapor manufacturing applications, hundreds of kilograms of material may be evaporated in a single production run. Under these conditions, thin film crystal devices and electron impact fluorescence monitors have inadequate life. Hollow cathode lamp monitors tend to saturate at high vapor densities and are susceptible to loss of calibration due to condensate buildup. Techniques such as emission spectroscopy are difficult because of extremely high background light levels and tend to provide only relative measures of density and composition.

Lawrence Livermore National Laboratory, 3M Corporation, New Focus Lasers Inc. and the Stanford University Center for Materials Research are participants in an Advanced Research Projects Agency (ARPA) sponsored collaboration to develop non-intrusive, laser based sensors and control technology needed for high rate vapor manufacturing applications. This paper reviews the principles of operation of laser based sensors and discusses data from experiments in which titanium and niobium are co-vaporized.

## 2.0 Principles of Operation

Principles of operation for a laser absorption spectroscopy vapor monitor have been previously reported[2]. Figure 1 schematically illustrates the technique. Light from a diode laser is frequency scanned over an atomic absorption line in the species to be monitored. The light is then acousto-optically modulated to improve noise rejection and to permit multiple lasers (each modulated at a different frequency) to be co-propagated along the same optical path. This permits simultaneous monitoring of multiple species. A portion of the light is split off from the beam and goes to a reference detector. This permits compensation for laser intensity fluctuations during the scan. The balance of the light enters the vapor, is partially absorbed and finally is detected at the exit from the vacuum chamber. The vapor density along the path of the laser is related to the attenuation of laser light by Beer's law,

$$I = I_0 e^{-n\sigma l}$$

where  $I$  and  $I_0$  are input and output laser intensities,  $n$  is vapor atom density,  $\sigma$  is the absorption cross section for the selected transition and  $l$  is beam pathlength through the vapor. Berzins discusses the methodology for transition selection and cross section measurement in a related paper in these proceedings[3].

A typical absorption waveform, in this case for the ground state of iron vapor, is shown in Figure 2. The waveform in Figure 2 is actually much broader than the natural line width of the iron transition. This is due to a Doppler broadening of the absorption line caused by the expansion velocity of the vapor. The laser can be scanned over all the vapor along the laser path, including that which is Doppler shifted. By scanning the laser

past the absorption line, a new baseline is established for each scan. This reduces the sensitivity of the monitor to window darkening caused by vapor deposition.

The actual device is shown in Figure 3. The light source is a New Focus external cavity tunable diode laser. The optical transport, signal detection and signal processing systems were designed by LLNL. Processing of the waveforms is currently done on an IBM PC. Density sampling rates up to 4 Hz have been demonstrated. In our installation at LLNL, the diode laser is in a different room from the vaporizer. Light is carried to the vessel by fiber optics. All optical transport and detection hardware are outside of the vaporizer vacuum vessel. Optical windows on the vessel are protected from vapor deposition by proper placement and by gas scattering cells.

### **3.0 Application to High Rate Vapor Phase Manufacturing**

Figure 4 summarizes the laser requirements needed to monitor the elements of the periodic table. Most of lanthanides and actinides can be monitored with lasers that operate at wavelengths greater than 6500 Å. Off-the-shelf diode lasers can be purchased that operate in this wavelength range.

Extending this monitoring technology to elements such as titanium and aluminum requires lasers that operate at shorter wavelengths than available from commercial tunable diode lasers. Numerous coating applications would benefit from the shorter wavelength vapor monitors: metal matrix composite manufacturing (Ti, Al, Nb, Mo), high temperature superconductors (Cu, Ba), thin film photovoltaics (Cu, In, Se) and turbine coatings (Cr). New Focus Lasers is developing the frequency doubling methods to extend the wavelength range available from diode lasers.

At LLNL, experimental work has concentrated on demonstrating the feasibility of monitoring the relevant elements and on developing evaporation control techniques. Feasibility demonstrations are performed using tunable light from argon ion pumped dye lasers and frequency doubled titanium sapphire lasers. These lasers provide a very broad wavelength range but are more difficult to operate than diode lasers in an industrial monitoring system.

Figure 5 shows laser data from an experiment in which titanium wire was fed into a niobium pool. Because the titanium vapor pressure is roughly four orders of magnitude greater than niobium, the titanium flash evaporates from the niobium pool. Evaporation rate of the titanium should closely track its feed rate. Figure 5 confirms the tight coupling between the titanium wire feed rate and the titanium density in the vapor.

Several frozen film samples were analyzed to illustrate the temporal variations in niobium and titanium vapor concentrations. Figure 6 illustrates the correlation between the Auger scan over the indicated feature in the micrograph and the laser data taken during the corresponding time during the run. The peak Ti vapor density was scaled to match the peak in the Auger scan and the distance scale in the Auger scan is set to match the time scale of the Ti vapor density plot. Therefore it is the comparison of the shapes of the two curves which is significant not the absolute correspondence between the curves. Nonetheless the match is impressive and leaves little doubt that the diagnostic laser provides a good indication of the concentration profiles in the deposited film.

Figures 7 and 8 pertain to an experiment with separate vapor sources for the titanium and niobium. Figure 7 shows the configuration. Relative evaporation rate for the two sources was varied and vapor deposits were collected on a movable wheel which was indexed each time the evaporation rates were changed. Titanium and niobium vapor densities



were monitored throughout the run. This allows a comparison between the chemistry of the deposit collected on the wheel with the composition measured by the vapor monitor. The vaporizer was equipped to wire feed aluminum into the titanium pool. However, aluminum density was not monitored during these experiments.

Figure 8 shows the Ti/Nb atomic ratio as a function of the power split between the titanium and niobium vapor sources. Deposit chemistry and laser measurements are both shown on the plot. In most cases, the agreement between the laser and the deposit chemistry is quite good. The data covers a very broad range of atomic ratios. In a practical control application, the dynamic range of atomic ratios would likely be much less. This would permit precision calibration of the vapor monitor.

#### 4.0 Summary

We believe that we are well along the path toward developing a practical, laser based vapor rate and composition monitoring system for electron beam PVD. LLNL has demonstrated monitoring feasibility for titanium and niobium and New Focus Lasers is developing the laser technology needed to monitor a broad range of commercially relevant materials. A goal of the ARPA sponsored program is to eventually make this technology commercially available as a fully integrated vapor monitoring system. A vapor monitoring demonstration at a commercial site is planned for 1995.

If successful, the development and commercialization of this technology can have far reaching benefits to the high rate PVD community.

## 5.0 References

1. R.J. Hill, Physical Vapor Deposition, Temescal Corp., T-0186-6001-1, 1986.
2. J. Galkowski and K. Hagans, Laser Absorption Spectroscopy System for Vaporization Process Characterization and Control, SPIE Proceedings, Optical Tools for Manufacturing and Advanced Automation, Boston, Ma., Sept. 7, 1993.
3. L.V. Berzins, et. al., Diode Laser Absorption Spectroscopy for Process Control - Sensor System Design Methodology, Metallurgical Coatings and Thin Films 1995, Elsevier.

## Figure Captions

### Figure 1

Schematic illustration of vapor density monitoring technique.

### Figure 2

Typical absorption waveform.

### Figure 3

Prototype of diode laser based vapor monitor.

### Figure 4

Wavelength requirements for laser based vapor monitors.

### Figure 5

Measured titanium vapor density compared to relative titanium feed rate.

### Figure 6

Comparison of frozen film titanium concentration profile and titanium vapor density history.

### Figure 7

Configuration for two vapor source experiments.

### Figure 8

Comparison between laser and deposit chemistry as a function of power split to titanium vapor source.

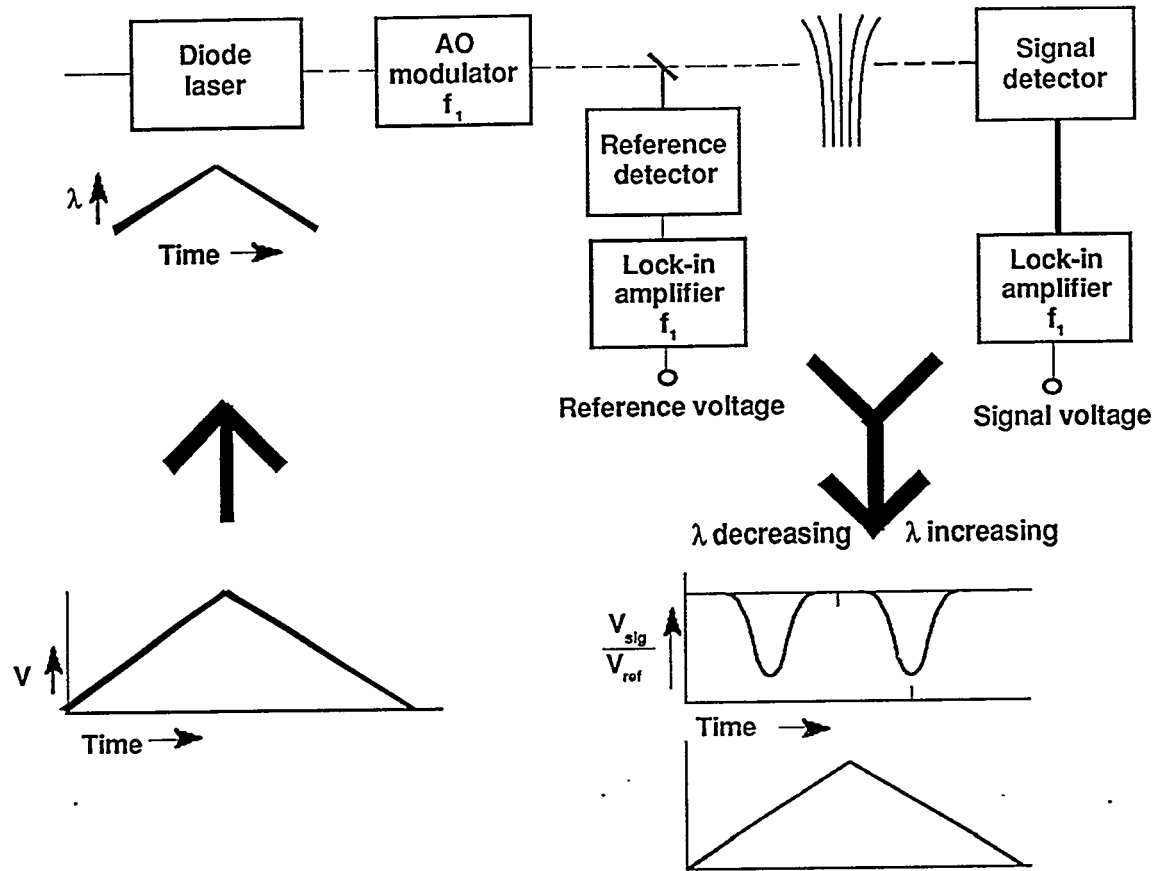


figure 1

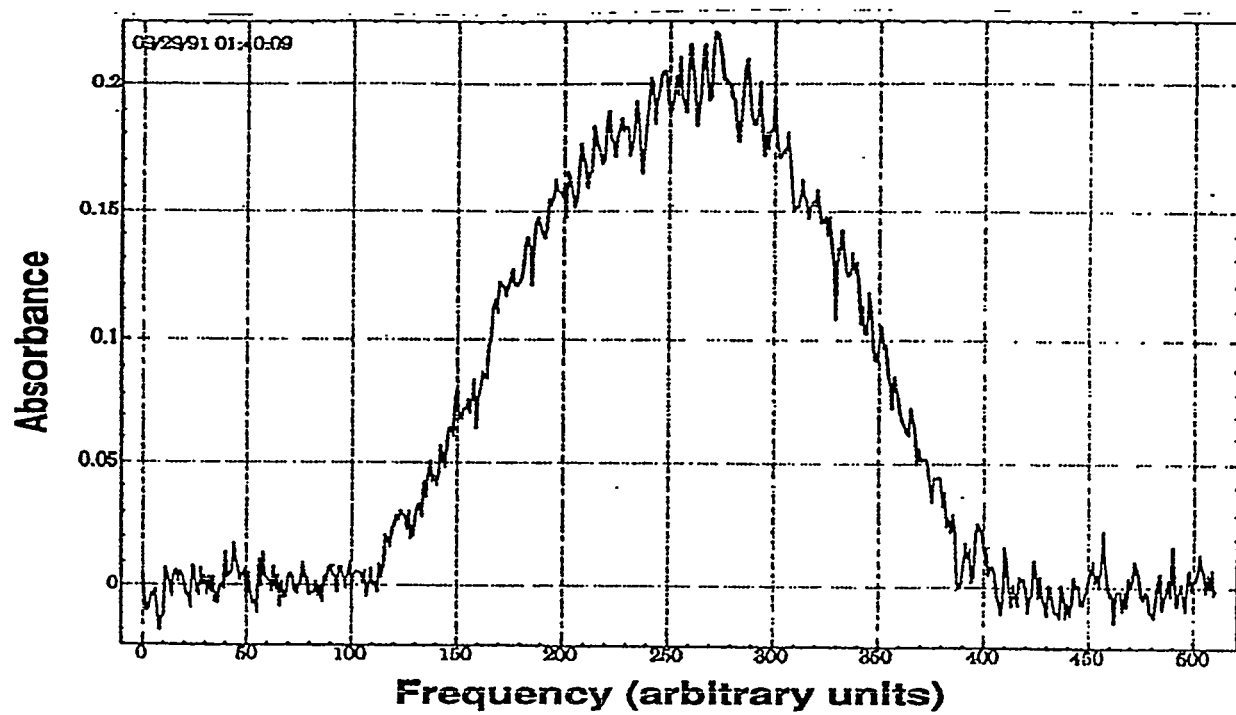


figure 2

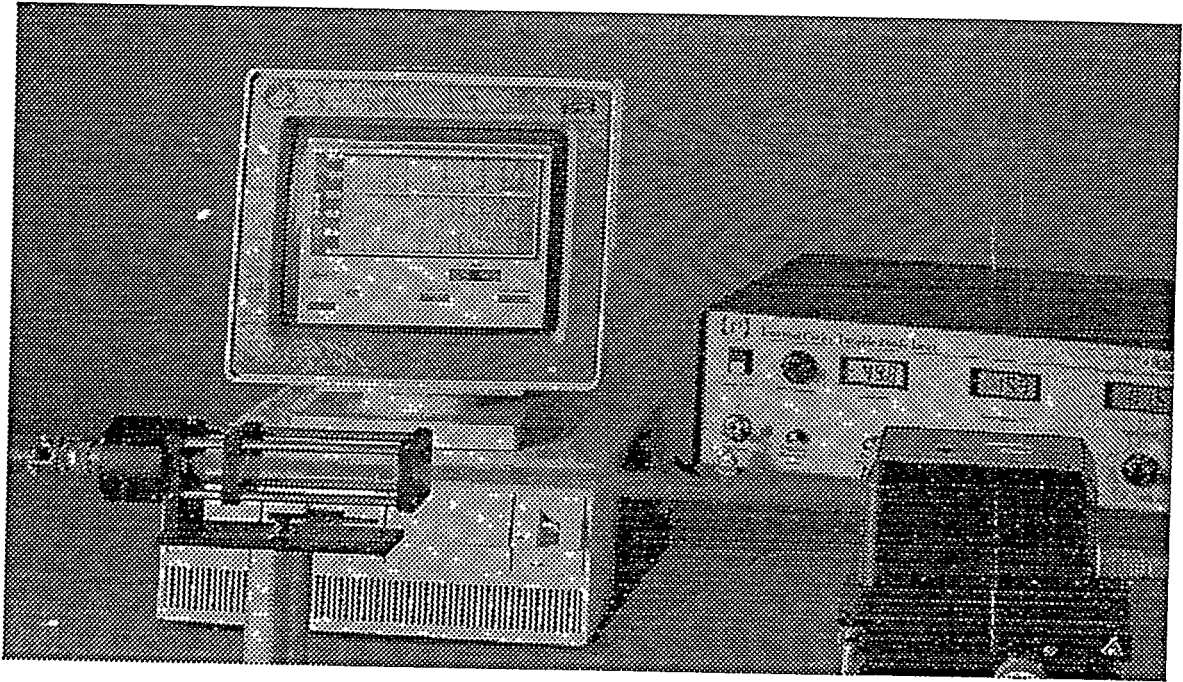


figure 3

# Longest wavelength ground state transitions for periodic table

1 H NS																	2 He NS
3 Li	4 Be											5 B	6 C	7 N NS	8 O NS	9 F NS	10 Ne NS
11 Na	12 Mg											13 Al	14 Si	15 P	16 S NS	17 Cl NS	18 Ar NS
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br NS	36 Kr NS
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I NS	54 Xe NS
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po NS	85 At NS	86 Rn NS
87 Fr NS	88 Ra NS	89 Ac NS															

58 Ce	59 Pr	60 Nd	61 Pm NS	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa NS	92 U											

figure 4

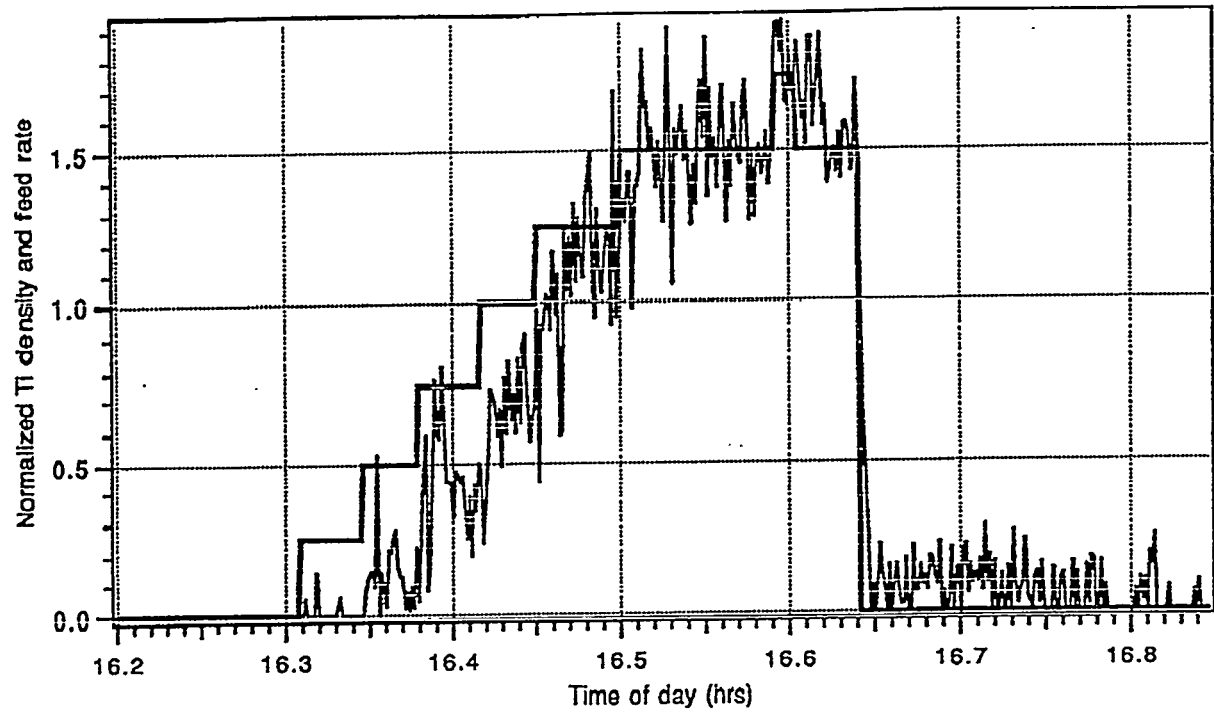


figure 5



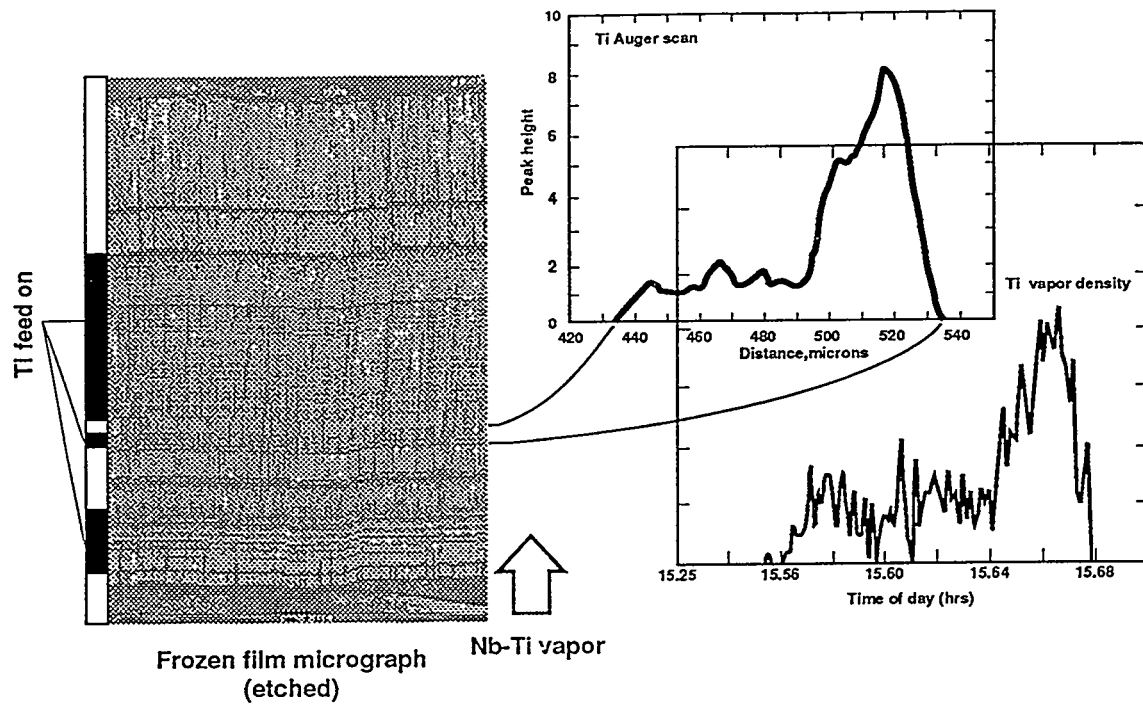


figure 6

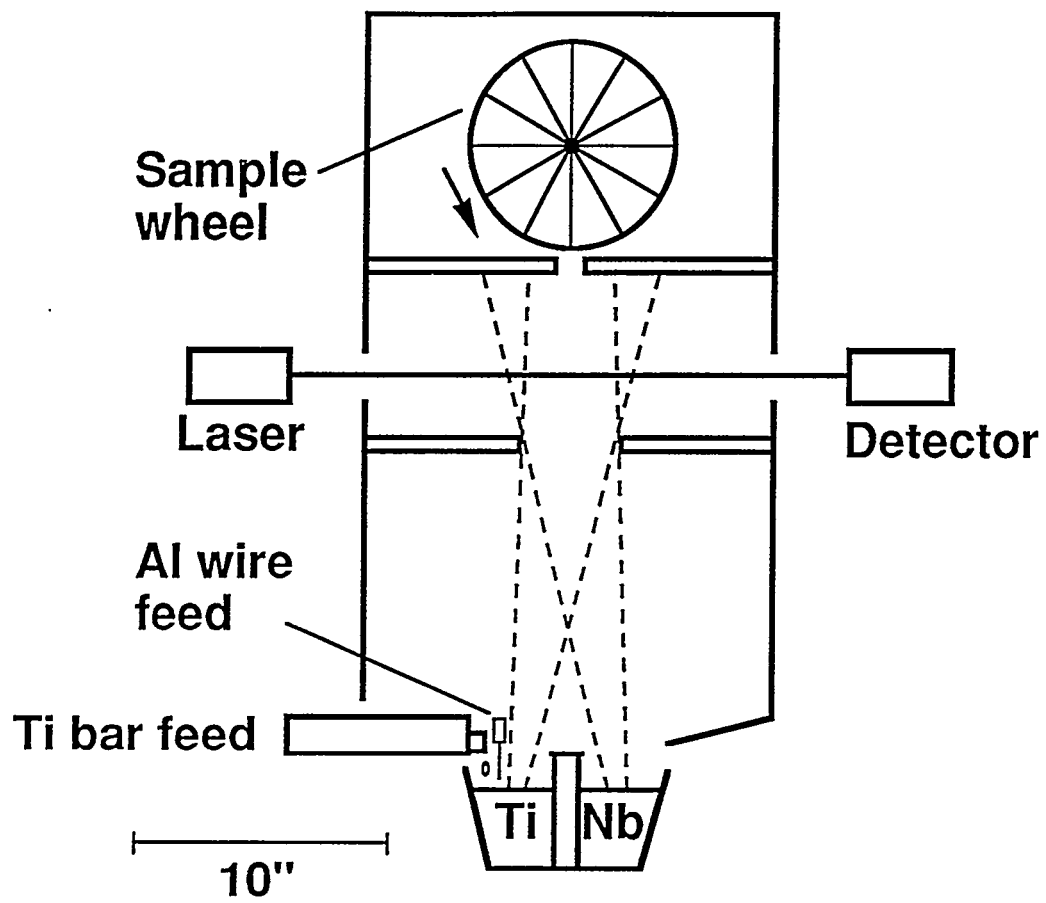


figure 7

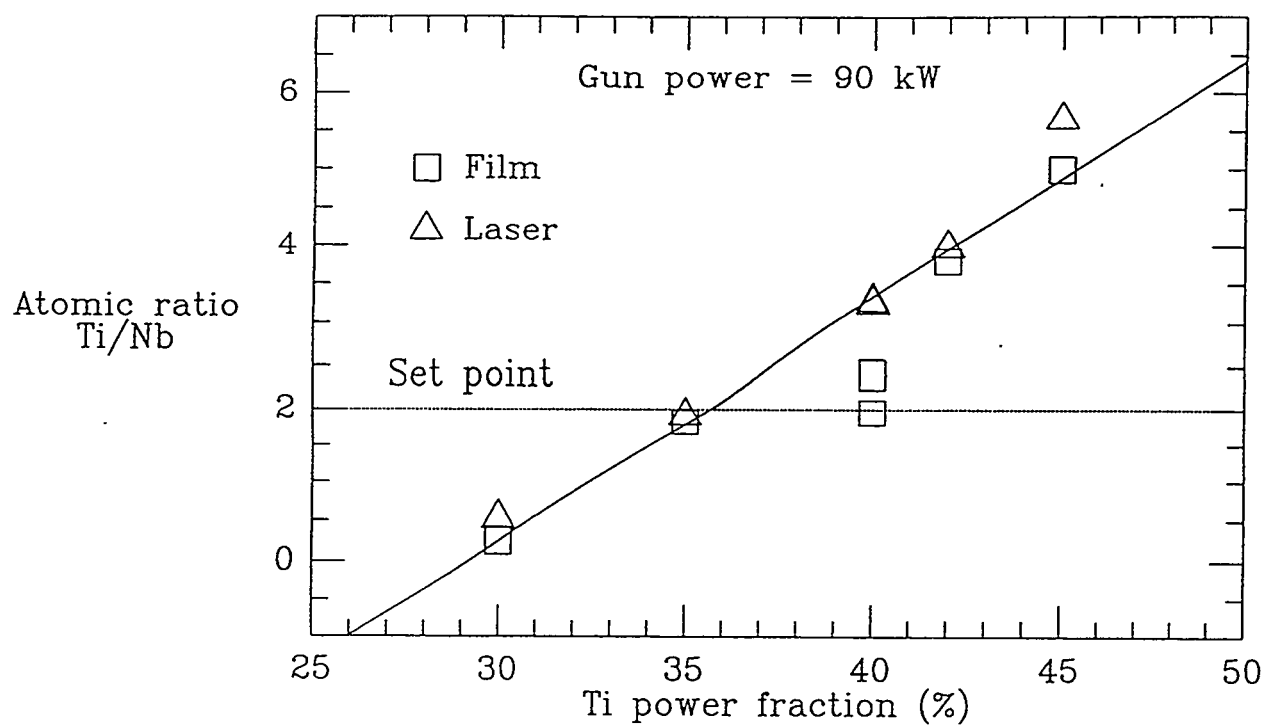


figure 8