

# Dual beam atomic absorption spectroscopy for controlling thin film deposition rates

S. J. Benerofe, C. H. Ahn, M. M. Wang, K. E. Kihlstrom,<sup>a)</sup> K. B. Do, S. B. Arnason, M. M. Fejer, T. H. Geballe, M. R. Beasley, and R. H. Hammond  
Edward L. Ginzton Laboratory, Stanford University, Stanford, California 94305

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We have developed a stable ( $<1\%$  drift/h at  $1 \text{ \AA/s}$ ), fast ( $\sim 200 \text{ ms}$ ), sensitive ( $S/N \sim 10\text{--}200$  at  $1 \text{ \AA/s}$ ) evaporation rate monitor for controlling electron beam sources. Based on dual beam atomic absorption spectroscopy (AAS), in which a reference arm compensates for drift in the light source and signal detection apparatus, this technique is very wavelength and hence element specific, allowing many elements to be simultaneously and independently monitored. Furthermore, the system can operate at very high background gas pressures, as well as under ultrahigh vacuum conditions. Also, because only the light must enter the vacuum chamber and pass through the evaporant, minimal periodic maintenance inside the chamber is necessary. The versatility and sensitivity of this AA system make it a viable candidate for *in situ* monitoring of various other thin film processes, including sputtering, ion milling, and reactive ion etching.

## I. INTRODUCTION

The discovery of high-temperature superconductors and related oxides has posed many challenges to thin film deposition techniques because of the demanding conditions under which these materials must be grown, specifically high oxygen partial pressures and very accurate composition control, on the order of  $1\%$ .<sup>1,2</sup> One persistent difficulty has been that most existing deposition rate monitors either do not operate well at high gas pressures or do not have sufficient sensitivity to control the deposition rates of individual elements within the desired accuracy.

To address this problem, we have developed a stable, fast, sensitive evaporation rate monitor based on dual beam atomic absorption spectroscopy (AAS) that can operate at high background pressures and is extremely element selective. Because this rate monitor is versatile and does not have to be placed inside the vacuum chamber, it is potentially applicable to a variety of thin film processes, including those used in semiconductor manufacturing, like sputter deposition and endpoint detection for ion milling.<sup>3-6</sup> It may also be useful for reactive ion etching and chemical vapor deposition, provided the modifications necessary for accurately detecting molecular species can be implemented.<sup>7</sup> In many of these processes, either stringent performance requirements or harsh operating environments preclude the use of traditional rate monitoring instruments.

The system that we have developed is a modification of an AA monitor developed by Lu.<sup>8</sup> In the earlier system, a single beam for the element to be monitored was generated by a hollow cathode lamp and passed through the evaporation flux. The attenuated signal was then measured with a photomultiplier tube (PMT). From Beer's law ( $I = I_0 e^{-n\sigma l}$ , where  $I$  is the transmitted intensity,  $I_0$  is the initial intensity,  $n$  is the density of the evaporant,  $\sigma$  is the photon absorption cross section, and  $l$  is the path length), the evaporation rate

could then be determined, in principle. However, this single beam approach is very susceptible to lamp and PMT drift, often on the order of  $10\%/h$  of the evaporation signal. To alleviate this problem, we have employed a dual beam approach, in which a beam-split reference arm travels around the vacuum chamber and is detected on the same PMT used for the signal arm. This two channel system eliminates drift from the light source and detection apparatus. We note that Klausmeier-Brown *et al.* have developed a variant, called pseudodouble beam AAS, that allows one to monitor, but not directly feed back to evaporation sources.<sup>2</sup>

To test our technique, we have grown epitaxial films of the ferromagnetic perovskite  $\text{SrRuO}_3$ . Both the structural and electronic properties agree well with existing work on bulk crystals and thin films; these results will be published elsewhere.

## II. INSTRUMENTATION

The atomic absorption setup is installed on a multiple source electron beam evaporator equipped with an ECR atomic oxygen source, and is shown schematically in Fig. 1. Radiation from a hollow cathode lamp (Hamamatsu L233) is focused into a  $1 \text{ mm}$  fused silica fiber, which acts to smooth the spatial variations of the lamp output through mode mixing in the fiber. This light is coupled back out of the fiber and passed through a beam splitter that generates the signal and reference light beams, which are then each chopped at a different frequency and coupled back into separate fibers. The signal light is fed into the chamber through a vacuum bellows containing an UV collimating lens and window. The radiation then travels through the evaporant plume adjacent to the sample stage, which is located  $38 \text{ cm}$  above the electron guns, and is coupled out of the chamber through another window, lens, and bellows assembly. To protect the windows from scattered evaporant,  $2.5 \text{ cm}$  long,  $1 \text{ cm}$  diameter chimney baffles are placed on the entrance and exit ports, which are spaced  $10 \text{ cm}$  apart. In order to reduce mechanical drifts

<sup>a)</sup>Permanent address: Dept. of Chemistry and Physics, Westmont College, Santa Barbara, CA 93108.

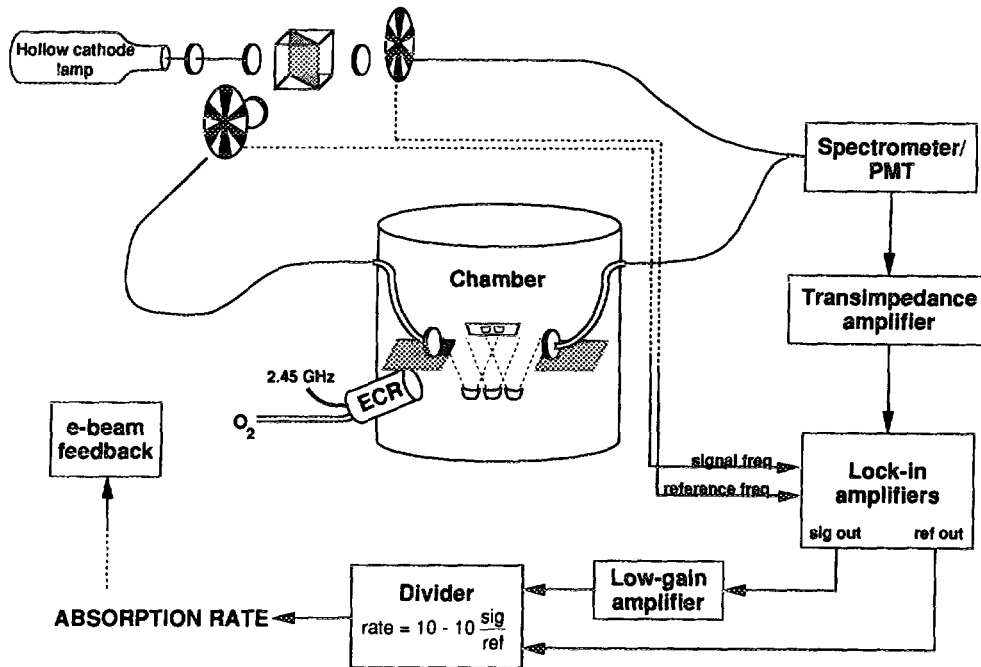


FIG. 1. Schematic of the AA setup.

due to thermal expansion, a water-cooled heat shield surrounds the bellows assembly and is used during evaporation of refractory materials like Ru.

The reference and signal arms are coupled into a spectrometer and a PMT (Hamamatsu R928).<sup>9</sup> The output of the PMT is amplified using a transimpedance amplifier (OPO7 op amp) with a 1 M $\Omega$  feedback resistor and sent into two lock-in amplifiers (Evans model 4110), where the signal and reference are demodulated. To normalize out lamp and PMT drift, the signal is divided by the reference in an AD 734BQ divider chip. Afterwards, some simple arithmetic is performed so that an AA output of 0 V corresponds to zero evaporation and attenuation, and 10 V corresponds to 100% attenuation of the signal, i.e. AA output (V) = 10 V - (10V) \* (signal/reference). Because the signal and reference arms typically do not have the same intensity due to differing losses in each arm, a low gain amplifier is used at the input of the divider to zero the AA output prior to beginning a deposition. At present, the electronics are configured to give a system bandwidth of  $\sim 5$  Hz, which is sufficiently larger than the bandwidth of the filament ( $< 1$  Hz) to attain good control in our evaporation system.

### III. RESULTS AND DISCUSSION

In order to study the performance of the dual beam AA system, we have grown samples of SrRuO<sub>3</sub> at  $\sim 4$  Å/s in a background pressure of  $1-2 \times 10^{-5}$  Torr of oxygen, with the pressure at the substrate itself in the millitorr region. The deposition of this material provides a good test of the AA system because of the high gas pressures involved, and also because Ru is a refractory material with very low photon absorption cross section. In Fig. 2, we show a typical chart recorder trace for one of our evaporation runs, which shows

the sensitivity and drift of the system. For Sr, the S/N ratio is  $\sim 200$  with a total drift of  $\sim 0.5\%$  of the signal at the end of the run, while for Ru, the S/N ratio is  $\sim 20$ , with drift of  $\sim 3\%$ . For both elements, the drift is caused by thermal expansion of the optical components that occurs when evaporating Ru, which reaches temperatures around 2500 K. Less than 1% drift is observed when depositing films that do not contain refractory elements (e.g., SrCuO<sub>2</sub> and SrC<sub>60</sub>). Also,

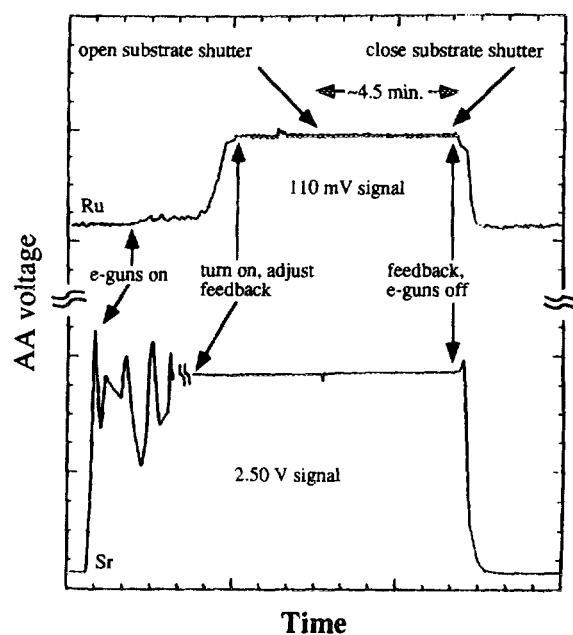


FIG. 2. Chart recorder trace for the growth of SrRuO<sub>3</sub>. The two traces are offset for clarity, and the scale for Ru is 10 times that for Sr.

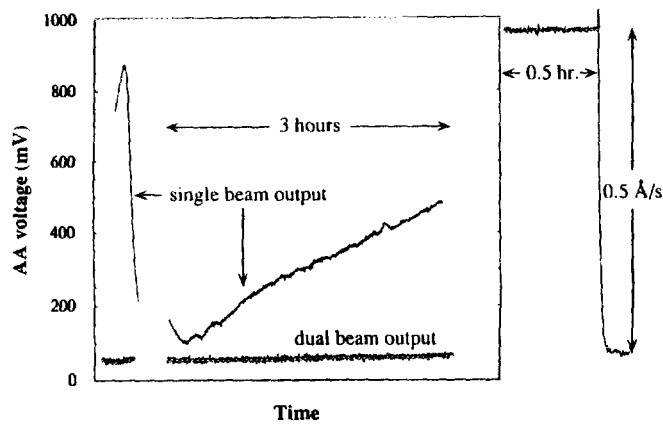


FIG. 3. Comparison of single beam and dual beam AA (offset for clarity). The left traces are 20 min long, and the right traces are 3 h long. To the right of the graph is a trace of Sr evaporating at 0.5 Å/s. The vertical scale is the same as in the graph.

we have determined that the noise in the system is attributable to the shot noise in the small ( $<1$  nW) optical signals. Finally, we can infer from Beer's law that the differences in the magnitude of the evaporation signal among various elements are caused by differences in photon absorption cross sections. As a result, while Ru has smaller noise because of higher output power from the Ru lamps, the  $S/N$  is actually smaller than that observed for Sr and other elements we have studied (e.g., see Cu in Fig. 4), due to its low photon absorption cross section.

We also note that in this particular run, we have set the bandwidth of the AA to  $\sim 0.5$  Hz, which is only comparable to that of the filament. This response time is acceptable, since we have observed that the bandwidths of the elemental sources themselves (Sr, Ru) are much smaller ( $\sim 0.1$  Hz) than that of the filament, which reduces the need for wide bandwidth feedback. In the case of temperature controlled Knudsen cells and nonreactive sputtering, which require no additional feedback, the bandwidth may be reduced substantially, allowing better  $S/N$  performance. The effect of feedback is apparent if one compares the right part of the Sr trace, where feedback was used, with the left part, where an operator manually controlled the rate.

In Fig. 3, we show the drift properties of the dual beam system more clearly, where we compare traces of single beam (unnormalized) and dual beam (normalized) AA outputs for Sr, with the electron guns off. Due primarily to lamp drift, the single beam AA exhibits drift of 650 mV in 20 min, which corresponds to a change in rate of  $\sim 0.4$  Å/s, whereas the dual beam setup shows less than 10 mV ( $\sim 0.006$  Å/s) drift. Over a longer period of 3 h, the total drift observed is still less than 0.006 Å/s.

While the data shown above demonstrate dual beam AAS to be a sensitive, low drift technique for controlling deposition rates, we have found that it is not as accurate at predicting rates, due to deviations from Beer's law absorption. The reason for these deviations is that the Doppler linewidth of the lamp emission ( $\sim 2$  GHz) is much broader than that of the evaporant atoms ( $\sim 0.5$  GHz). As a result, only a fraction

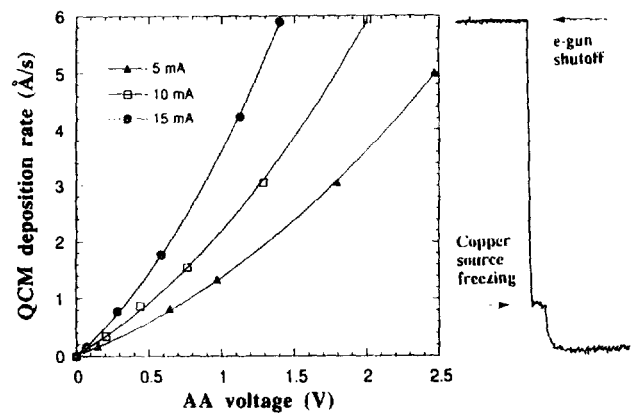


FIG. 4. QCM deposition rate vs Cu AA signal for various lamp currents. The lines are a guide to the eye. On the right is an AA trace for deposition at  $\sim 0.7$  Å/s. The noise is 1%–2% of the signal. The plateau after turning off the electron gun is the Cu source freezing.

of the radiation from the lamp can ever be absorbed by the evaporant, and absorption saturation occurs earlier than might be expected. This behavior becomes more evident at large lamp currents because of increases in self-absorption in the lamp. From Beer's law, noticeable deviations (1%) from linearity should occur at  $\sim 10\%$  absorption (1 V) in the absence of Doppler broadening, but can be seen to occur earlier in the data in Fig. 4, which shows the observed quartz crystal monitor (QCM) deposition rate versus AA voltage for 3 different lamp currents.<sup>10</sup> We note, though, that once such a curve is traced out empirically for a given lamp current using an absolute measurement like the QCM,<sup>11</sup> interpolation to any desired rate is straightforward. Furthermore, this calibration only needs to be carried out once; we have found that the deposition rate for a given AA voltage is reproducible on a daily basis to within 1%, which is the error in the QCM measurement. Some other rate monitors, including the quadrupole mass spectrometer, need frequent recalibration, as often as every run.<sup>12</sup>

The use of tunable lasers to replace hollow cathode lamps would not only eliminate this problem, since their linewidths are much narrower; one could also examine the Doppler broadening of the evaporant itself, as has been demonstrated by Berzins *et al.* using diode lasers and by Chalmers *et al.* using dye lasers.<sup>13,14</sup> In addition, lasers would make further developments based on standard optical techniques much easier to implement. For example, using frequency modulation (FM) spectroscopic techniques would compensate for light source and detector drift, as well as for changes in optical transmission due to thermal expansion and coating of the optics, without the need for a separate reference arm. The resulting simplification in the optics and detector, combined with the fact that hollow cathode lamps have a limited lifetime of  $\sim 1000$  h, could make systems based on tunable diode lasers an economically competitive option in the future, although limitations on their frequency range may not allow them to monitor certain elements, like those that only have ultraviolet transitions.

In summary, we have developed a fast, sensitive evaporation rate monitor for controlling deposition rates. We believe

that this technique is versatile and robust enough to be potentially useful for a variety of other thin film applications.

#### ACKNOWLEDGMENTS

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<sup>9</sup>It is important that the two light beams are focused onto the same region of the PMT's active area in order to accurately compensate for drifts in the detector's sensitivity.

<sup>10</sup>This deviation is also much larger than the nonlinearity introduced by the fact that the AA measures the density of the evaporant, and not the mass deposition flux. See Refs. 2 and 8.

<sup>11</sup>Even the QCM has a tooling factor and is thus not an absolute measurement. Furthermore, it is not element sensitive, nor can it distinguish between deposition of the pure element or its compound during reactive depositions.

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<sup>14</sup>S. A. Chalmers and K. P. Killeen, presented at the 13th North American Conference on Molecular-Beam Epitaxy, Stanford, CA, 13–15 September 1993 (unpublished).