Diode-laser-based atomic absorption monitor using frequency-modulation spectroscopy for physical vapor deposition process control

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We have developed an atomic monitoring system for physical vapor deposition process control based on a frequency-modulation (FM) spectroscopy scheme using a 670 nm external cavity diode laser. FM detection made it possible to measure absorption as low as 10^{-6}. For electron-beam evaporated yttrium, deposition rate control with a relative accuracy better than 1% at a rate of 3.5 Å/s has been realized, corresponding to a deposition rate resolution of 0.03 Å/s. Variations in Doppler shifts due to the velocity distribution of the atomic vapor within the deposition chamber have been measured, demonstrating the possibility of velocity mapping of evaporated atoms in the deposition process. © *1995 American Institute of Physics.*

Monitoring and control of physical vapor deposition (PVD) are required for a variety of deposition processes, including high-performance alloys, high-temperature superconductors, metallization of semiconductor devices, photovoltaic materials, and thermal barrier coatings. The development of nondestructive, species selective, and noninvasive monitoring and control systems is desirable for these purposes. In addition, there are many physical processes that occur during the deposition for which further understanding is helpful, such as quantitative, real time examination of the growth kinetics of thin films, and the dynamic events occurring as vapors condense on a substrate. Atomic absorption (AA) spectroscopy is a promising approach for these applications. Conventional light sources such as hollow cathode lamps (HCL) have limited utility in these applications because they are spatially incoherent and have low intensity and broad spectral width.[1] In contrast, laser spectroscopy offers an attractive alternative with high sensitivity and resolution. In particular, compact, highly stable external cavity diode lasers (ECDL) which are now commercially available facilitate these applications. Among various high sensitivity and high resolution approaches, the frequency-modulation (FM) spectroscopy technique has advantages, especially for detection of weak absorption.[2–4]

In this letter, we report an ECDL-based FM spectroscopy system for AA monitoring and closed-loop control in a vacuum deposition chamber. Yttrium evaporated from an electron beam source was used as a demonstration. Spatial variations in velocity of the atomic vapor have also been measured by means of the Doppler frequency shifts of the atomic absorption with respect to a HCL reference, which can be used for atomic velocity mapping in a PVD process.

Yttrium was chosen for our experiment because of its importance in the deposition of high-temperature superconductors. A transition at 668 nm, which is 2 orders of magnitude weaker than the one commonly used for AA (410 nm), was employed for its accessibility to available diode laser wavelengths. A visible ECDL (New Focus 6100), which can be tuned continuously over 15 nm around 670 nm with an output power of 6 mW, was employed as a light source. Figure 1 shows the configuration of the laser-based system. An electro-optic (EO) phase modulator is driven by a radio frequency (rf) source at 450 MHz to generate a pair of weak FM sidebands. Differential absorption of the sidebands is converted into an amplitude modulation signal at the modulation frequency, which is detected with a phase-sensitive detection scheme, eliminating noise contributions outside the detection band centered around the modulation frequency. For sufficiently high modulation frequency, the detection

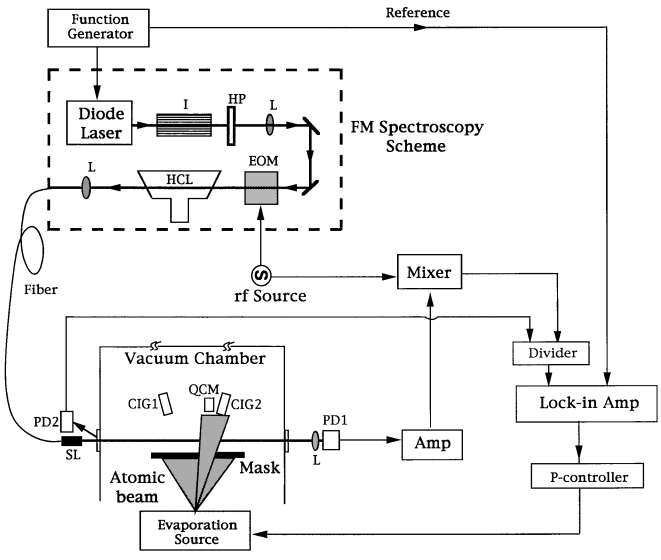

FIG. 1. Schematic of the diode-laser-based FM spectroscopy system for evaporation rate control in a deposition chamber. EOM, electro-optic modulator; HCL, hollow cathode lamp; L, lenses; SL, Selfoc lens; PD1, wideband photodetector; PD2, photodetector; CIG1,2, chopped ion-gauge monitors; QCM, quartz crystal monitor; I, optical isolator; HP, half-wave plate.

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sensitivity in the FM scheme is thus given by the shot-noise limit determined by the detected power rather than the excess low frequency noise of the laser source. To make the system compact and flexible, a single-mode optical fiber was used to deliver the laser beam into the vacuum deposition chamber. The laser beam was end-fire coupled to the fiber (with an efficiency of about 60%) using an objective lens. The output end of the fiber is connected to a Selfoc lens which collimates the laser beam to a diameter of 1 mm. The laser beam passing through the vacuum deposition chamber was focused onto a wideband photodetector (New Focus 1601) with a 50 mm lens. The system contains an yttrium HCL used as a reference for monitoring the laser frequency. It also provides an unshifted Doppler-broadened line shape reference for comparison with the line shape and line center shift obtained from the deposition chamber. The width of the absorption resonance in the HCL is about 1.3 GHz, calibrated by comparison with the free-spectral range of a 1-cm etalon.

To characterize the FM spectroscopy system, the HCL was driven at 400 Hz by an on/off modulated power supply, and the FM AA signal from the mixer was demodulated with a lock-in amplifier. Because the frequency of the modulation applied to the EO modulator is smaller than the width of the absorption resonance, the output signal from the rf mixer is approximately proportional to the first derivative of the absorption profile,[5] which can be expressed as

$$V_{\text{out}} = 4G(\omega)AP_{\text{in}}M\alpha_0\Gamma^2 \times \frac{(\omega-\Omega)\omega_m}{[(\omega-\Omega)^2+\Gamma^2+\omega_m^2]^2-4\omega_m^2(\omega-\Omega)^2},$$

where a Lorentzian line shape is assumed,[6] $G(\omega)$ [V/W] is the detector response, A [V/V] is the voltage gain of the amplifier, P_{in} [W] is the laser power incident on the detector, M is the modulation index, α_0 is the peak absorption in resonance, Γ is the half-width of the absorption resonance, Ω is the frequency of atomic absorption transition, ω is the laser frequency, and ω_m is the frequency of the rf modulation. The peak-to-peak output voltage from the mixer was measured to be 10 mV at an incident laser power of 0.5 mW, $\Gamma = 650$ MHz, $\omega_m = 450$ MHz, $A = 10^3$, and $G = 110$ V/W, while the absolute absorption in the HCL and the modulation index were measured independently to be 3×10^{-3} and 0.1, respectively. The signal-to-noise ratio obtained from the output of the lock-in amplifier (with a time constant of 100 ms) was measured to be about 1200, both by inserting a neutral density filter in front of the detector and by lowering the rf power applied to the EO modulator. This result implies that the minimum detectable absorption of our system at this power is below 10^{-6} when a detection bandwidth $\Delta f = 1$ Hz. The theoretical quantum limit of the detectable absorption difference seen by FM sidebands under the same conditions is $\Delta\alpha = (2\Delta f h\ \omega/\pi\ M^2\eta P_{\text{in}})^{1/2} = 6\times 10^{-7}$, where h represents Planck's constant, and the quantum efficiency of the detector $\eta = 0.08$.

For rate monitoring and control of the deposition process, it is convenient to use the second derivative of the absorption profile on line center. This signal is proportional to the peak absorption, while the first derivative of the absorption at this frequency is zero. As the FM output signal from the mixer provides the first derivative of the absorption profile, the second derivative can be obtained by dithering the laser frequency and demodulating the signal with a lock-in amplifier. The maximum output from the lock-in amplifier, which is proportional to the second derivative of the absorption profile on line center, can be expressed as $V_{\text{out2}} \propto P_{\text{in}} M\alpha_0\delta\omega\Gamma^2\omega_m/(\Gamma^2+\omega_m^2)^2$, where $\delta\omega$ is the dither amplitude of the laser frequency. In the experiment, the frequency dither was performed by driving a piezoelectric transducer attached to the external grating of the laser at 170 Hz.

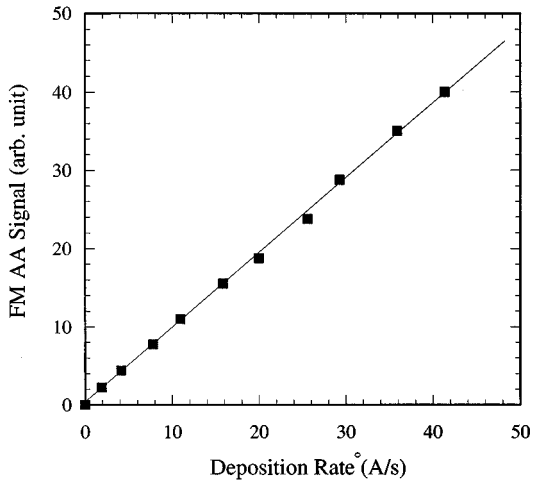

FIG. 2. Measured relationship between the FM AA signal and the evaporation rate measured independently by a quartz-crystal monitor.

To test the FM system, the second derivative signal was compared to the rate obtained with a quartz-crystal monitor (QCM). The relation between the FM AA signal and the QCM signal for electron-beam-evaporated yttrium is shown in Fig. 2. The rate was also measured independently by two chopped ion-gauge (CIG) monitors,[7] the results for all three monitors were consistent. The linear relation of the signal from the FM system and the QCM demonstrates the linearity of the present laser-based system over a range of 40 Å/s in deposition rate. In our experiment, there is no evidence of a change in the relative population for the presently used 668 nm transition and another sublevel of the ground state at 679 nm. In systems where the populations in these two sublevels change significantly, it may be necessary to monitor both transitions simultaneously.

In order to demonstrate closed-loop control of the deposition rate based on the laser-based AA system, we employed the second derivative of the absorption profile on line center for feedback. To eliminate the AM noise of the laser due to the frequency dither, we ratioed the second derivative signal with a signal proportional to the dc laser power measured with a second photodetector positioned in front of a beam that reflected off the input window of the vacuum deposition chamber. The error signal for the proportional controller, which was applied to the electron beam system, was the difference between this ratio signal and a set point. In Fig. 3, we show the FM AA signal along with the simultaneous outputs from two CIG monitors inside the chamber when the

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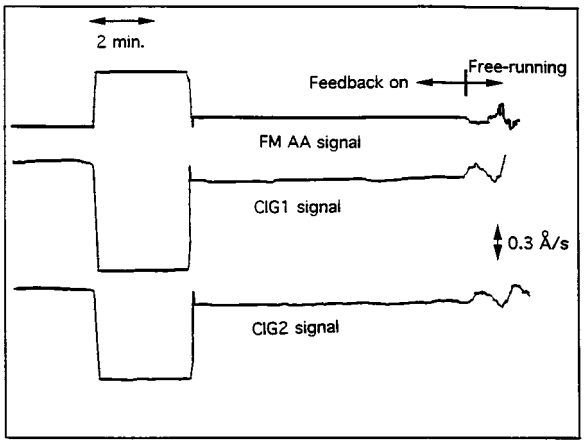

FIG. 3. The FM AA signal when this output signal was used for controlling the deposition rate of 3.5 Å/s, and the simultaneous output signals from the independent chopped ion-gauge (CIG) monitors. The FM AA signal is reversed in polarity with respect to the other signals. The steps in the chart-recorder traces correspond to changes in the set point.

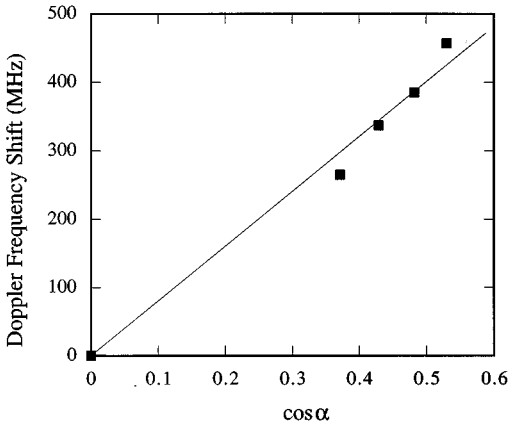

FIG. 4. Measured Doppler frequency shifts vs cos α, where α is the angle between the laser beam and the atomic beam.

yttrium deposition rate was 3.5 Å/s. This result shows that the deposition rate had relative residual fluctuations of less than 1%, implying a resolution of 0.03 Å/s. Such resolution is satisfactory for most applications.

The accuracy of the rate control in the present system is limited by the long term laser frequency drift and residual etalon effects which result in baseline variations in the FM signal.[3] The etalon effect in our FM system is caused by the reflections from various optical surfaces including the EO modulator, the optical fiber, the chamber windows, and the detector. All of these can be reduced by tilting the laser beam and using antireflection coatings. For further improvement of the accuracy in rate control and other diagnostic applications, the laser frequency drift can be circumvented either by using a computer-controlled frequency-swept measurement across the entire absorption resonance instead of using a fixed frequency as in the present scheme, or by locking the laser frequency to the HCL. Moreover, contamination of the chamber windows due to metal condensation, which also causes changes in the system transmission and therefore the FM signal, can be corrected by normalization to the average transmitted laser power obtained from the dc photocurrent of the wideband photodetector.

To demonstrate the feasibility of diagnosing the deposition process with the laser-based AA system, we measured the Doppler frequency shifts corresponding to different velocities in different parts of the atomic vapor. Because the velocities of the atomic vapor inside the chamber have a broad angular distribution, a mask in which different windows can be selected was used to aperture the atomic vapor. Atoms passing through different apertures in the mask have different angles with respect to the laser beam, and therefore, different Doppler frequency shifts. Figure 4 shows the measured Doppler shifts. The measurement was carried out by sweeping the laser frequency across the absorption resonance and comparing the absorption profiles observed in the atomic beam in the chamber and in the HCL. The measured value of the frequency shift is in agreement with the geometrically determined Doppler shift arising from the angular variations which in our case is proportional to cos α, where α is the angle between the laser beam and the atomic beam. This result shows that the present system can be used for mapping the velocity distribution of atoms in PVD processes.

Extension of this system to many technologically important species (e.g., Al, Ti, W, etc.) inaccessible to IR diode lasers requires visible or UV sources. Toward this end, we have recently demonstrated AA spectroscopy of aluminum using an ECDL diode laser frequency doubled in a quasiphase matched lithium niobate waveguide. Detailed results will be published elsewhere.

In summary, we have developed a 670 nm diode-laser-based FM AA spectroscopy system for thin-film process control. Electron-beam evaporated yttrium in a deposition chamber was used to demonstrate the system. FM detection made it possible to measure absorption as low as 10^{-6}. Deposition rate control with a relative accuracy better than 1% at a rate of 3.5 Å/s has been demonstrated, corresponding to a deposition rate resolution of 0.03 Å/s. Doppler shifts due to the velocity distribution of atomic beams in the deposition chamber have also been measured, demonstrating the utility of this high sensitivity, high resolution spectroscopic method as a diagnostic tool for PVD processes.

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