

The generation and detection of high flux atomic oxygen for physical vapor deposition thin film growth

N. J. C. Ingle,^{a)} R. H. Hammond, and M. R. Beasley
Department of Applied Physics, Stanford University, Stanford, California 94305

D. H. A. Blank
Department of Applied Physics, University of Twente, Enschede, The Netherlands

(Received 21 June 1999; accepted for publication 29 October 1999)

The growth of many epitaxial thin-film oxides is significantly enhanced with the use of an oxidizing agent such as atomic oxygen, ozone, or NO₂. We developed a flow-through microwave plasma source to generate large atomic oxygen fluxes while maintaining vacuum pressures of less than 1×10^{-4} Torr. Continuous and real-time detection of the atomic oxygen was achieved by atomic absorption of the 130 nm atomic oxygen lines. Atomic oxygen fluxes of at least 1.4×10^{18} atoms/cm² s and dissociation efficiencies of around 100% were obtained. © 1999 American Institute of Physics. [S0003-6951(99)00952-3]

In recent years there has been growing interest in complex oxides that can only be grown in the bulk phase under high oxygen pressure, or that require the addition of oxygen after growth with techniques such as electrolysis. The growth of these materials in thin-film form offers many advantages for certain experiments and is required for device applications.

Typically, ozone,¹⁻³ NO₂,^{4,5} or radio frequency (rf) and electron cyclotron resonance (ECR) atomic oxygen sources⁶⁻⁸ have been used to generate highly active oxygen for thin-film deposition of many oxides. The generic ECR and rf atomic oxygen sources, while easy to operate, are intrinsically limited to low fluxes of atomic oxygen and can generate some energetic ionized oxygen which may be unwanted. Ozone and NO₂ are both “gentle” forms of highly active oxygen. However, the oxidizing ability of ozone strongly depends on what reaction is occurring on the surface of the film⁹ and NO₂ has a lower oxidation ability than ozone or atomic oxygen.⁹ Beyond these materials issues, ozone is explosive at higher concentrations and NO₂ is highly toxic, requiring special gas handling equipment.

The design of the flow-through microwave plasma source (FTMP) described in this letter, in combination with our specific chamber configuration (pumping speed of 4000 L/s), is intended to allow high flow rates, good coupling between the plasma and the microwave cavity, and the ability to use high power all in an effort to generate very high fluxes of atomic oxygen while minimizing the production of energetic ionized oxygen and keeping the pressure of our chamber at below 1×10^{-4} Torr. The use of high flow rates to achieve high fluxes is required since, for example, a flow of 1 sccm of O₂ will only allow the generation of a flux of 4×10^{16} atomic oxygen atoms/cm² s assuming a source with a 100% dissociation efficiency, a fully collimated 0.025 m diam beam, and room-temperature thermal velocity. The primary disadvantage of this source is a weak correlation between the readily measurable parameters, such as microwave power or gas flow rate, and the actual production of atomic oxygen. For this reason, we have pursued various alterna-

tives to measure the atomic oxygen output. In this letter, we use atomic absorption (AA), a noninvasive and real-time detection scheme, and the oxidation of silver-coated quartz-crystal rate monitor (QCM) to determine the atomic oxygen flux.

Figure 1 shows a schematic of the atomic oxygen generation and detection setup. Astex Microwave equipment used to generate the atomic oxygen included the following: AX2115-Generator; AX3120-Circulator; AX3030-Dummy Load; AX3041-3 Stub Tuner; and AX7020-Downstream Plasma Source. Several modifications were made to the downstream plasma source to accommodate cooling of the quartz plasma confinement tube with coaxial flowing N₂ gas. Gas mixtures were allowed into the plasma confinement tube after passing through individual leak valves preceded by Sierra Instruments Series 820 Top-Trak™ flow monitors. In these experiments the total length of the quartz plasma confinement tube and the Teflon-coated delivery tube was never changed (1 m), however, the ratio of the total length that was quartz or Teflon coated was varied as described later in this letter.

An oxygen discharge lamp from Resonance, Ltd., was used as the light source for the atomic absorption. A CsI photodetector, also from Resonance, Ltd., with a detection bandwidth from 110 to 220 nm detected two atomic oxygen

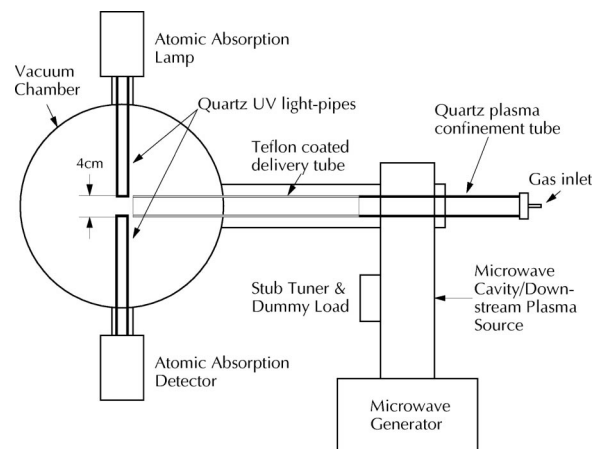


FIG. 1. Configuration of the atomic oxygen generation and detection scheme.

^{a)}Electronic mail: ingle@loki.stanford.edu

lines; the triplet 1302–1306 Å lines ($2s^22p^4\ ^3P - 2s^22p^33s\ ^3S_1$), a dipole-allowed transition, and the doublet 1356–1359 Å lines ($2s^22p^4\ ^3P - 2s^22p^33s\ ^5S_2$), a dipole-forbidden transition. The intensity ratio of the dipole-forbidden 1356 Å doublet lines to that of the 1302–1306 Å triplet lines was measured to be 0.48. Beer's Law in the form $I - I_b = (I_o - I_b) \sum_{j=0}^2 R_j \exp(-\sigma_j n_j l)$ takes into account the triplet absorbing lines, the nonabsorbed background lines (1356 Å), and allows the atomic oxygen density n_o to be calculated.¹⁰ I is the intensity incident on the detector after absorption, I_o is the total intensity generated by the lamp, $I_b = 0.48I_o$ is the intensity of the nonabsorbed 1356 Å emission, R_j is the relative intensity ratios of the triplet lines, n_j is the number density of $O(^3P_j)$ atoms from which we calculate n_o ,¹⁰ σ_j is the absorption cross section for each of the 1302–1306 Å triple lines which are assumed identical, and l is the absorbing path length. Several values of the atomic oxygen absorption cross section have been published for the 1302–1305 Å lines.^{11–13} We use an average value of $\sigma_j = 1.4 \times 10^{-13}$ for this letter. With a path length of 0.025 m the largest detectable density is $2.0 \pm 0.62 \times 10^{13}$ cm⁻³, assuming our minimum detectable intensity is determined by the detector noise.

The 0.025 m path length required the use of a low-loss delivery medium as the lamp and detector could not be mounted inside the chamber. Due to the large absorption of the far-UV light with standard solid-core glass fibers, we used a hollow-core waveguide, or light pipe. The most ideal situation for a hollow-core waveguide at this wavelength would be an Al coating on the inside of quartz tubes which are inherently smooth. However, the bare quartz tube was good enough, and more convenient, for our purposes. A similar procedure for manipulating far-UV light was recently published by Matsuura and Miyagi.¹⁴

The atomic oxygen flux is calculated ($\Gamma = n_o v$) from the atomic oxygen density obtained from Beer's Law and a velocity which we assume to be the room-temperature thermal velocity $v = 6.8 \times 10^4$ cm s⁻¹. This assumption is valid due to the long length of our delivery tube which allows many wall collisions to occur.

Figure 2 shows the effect of gas flow rate and microwave power on the flux of atomic oxygen generated with our flow-through microwave power source and detected with the AA. The dotted line at 1.4×10^{18} atoms/cm² s is the maximum detectable flux for the 0.025 m path length. The gas flow rate has the largest effect on the amount of atomic oxygen generated. However, a flow rate of 150 sccm corresponds to a pressure of 7.4×10^{-4} Torr in our chamber, which is unacceptable for molecular beam epitaxy-like deposition conditions. We are limited to flow rates of 50 sccm to maintain a chamber pressure of 1×10^{-4} Torr. With lower flow rates the dissociation efficiency¹⁵ is largest, ~100% for a 10 sccm flow of O₂ and 700 W microwave power. The dissociation efficiency for a 50 sccm flow of O₂ and 400 W, giving a similar flux, is only ~22%. At all the measured microwave powers and flow rates the ion current, as observed via a faraday cup, was below the detection limit of 0.15 μA cm².

Table I shows the effects of changing the ratio of quartz confinement tube to Teflon-coated delivery tube and of gas

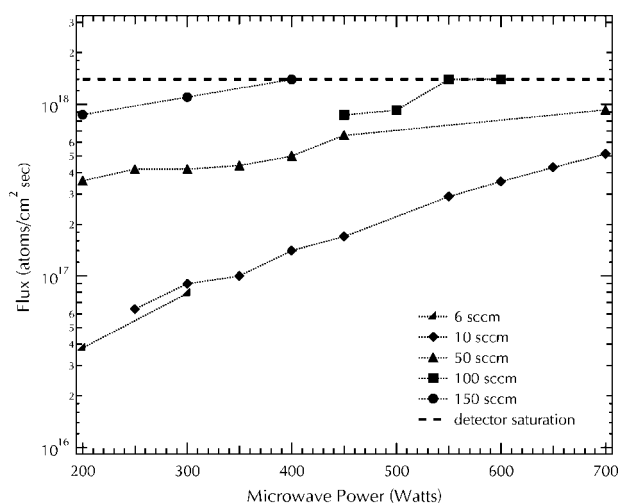


FIG. 2. Atomic absorption measurements of the flux of atomic oxygen as a function of microwave power and O₂ flow rate for the flow-through microwave power (FTMP) source.

composition on the production of atomic oxygen as determined by the AA. Configuration 1, in Table I, is a 0.25 m quartz plasma confinement tube and 0.75 m of teflon coated delivery tube. At higher flow rates (above 30 sccm) the plasma tends to form higher up in the quartz plasma confinement tube, and on occasion melted the first several centimeters of the teflon coating in the delivery tube. To minimize this damage we increased the length of the plasma confinement tube by using a quartz tube to replace the first 0.15 m of the Teflon coating on the delivery tube (configuration 2, in Table I). This caused the flux of atomic oxygen measured by the AA to drop by about 35%. Replacement of this 0.15 m quartz tube with a 0.05 m quartz tube with a boric acid surface treatment,¹⁶ with the remaining 0.10 m coated with Teflon again (configuration 3), increased the AA measured flux by a factor of 2.5 with respect to the initial arrangement (configuration 1). If the quartz plasma confinement tube is also given a boric acid treatment (configuration 4) we find an increase of a factor of ~4 with respect to configuration 1.

Yu-Jahns *et al.*¹⁸ showed that the addition of impurity gases to the O₂ increased the production of atomic oxygen. As shown in Table I, we found no appreciable difference to the atomic oxygen flux with the addition of ~1 sccm of He, however, we found a factor of 5 increase in the flux of atomic oxygen when a small amount (≤ 0.1 sccm) of N₂, H₂ or air was added in configuration 2. With configuration 4, the "complete boric acid" setup, only a 30% increase was seen with the addition of ≤ 0.1 sccm of H₂ or air. Yu-Jahns *et al.*¹⁸ found no change in the optical emission spectroscopy of the plasma with the addition of N₂ or H₂O, suggesting the addition of impurities does not catalyze the dissociation of oxygen, but causes a reduction in the surface recombination. Our results support this hypothesis because the gas composition effects and the surface coating on the plasma confinement tube effects are not additive, suggesting they are both influencing the same property.

As suggested by the greater than 100% calculated dissociation efficiencies shown in Table I, the atomic absorption detection scheme may not be the best absolute measure of the atomic oxygen flux until more is learned. Any uncertainty in the absorption cross section will give a large uncertainty in the calculated flux, and the published values for the

TABLE I. Atomic oxygen flux and dissociation efficiency (see Ref. 15) measured by atomic absorption for various plasma confinement tube configurations and gas compositions. Uncertainties are calculated based on the detection system noise, they do not account for uncertainties associated with the atomic oxygen cross section or relative intensity ratios in the oxygen discharge lamp. Please see the main text for a discussion on the greater than 100% dissociation efficiencies and for a description of the four different configurations.

Configuration	Gas	Flow (sccm)	Power (W)	Flux (atoms/cm ² s)	dissociation (%)
1	O ₂	10	300	1.1 ± 0.2 × 10 ¹⁷	21–30
2	O ₂	10	300	0.7 ± 0.01 × 10 ¹⁷	10–21
3	O ₂	10	300	2.8 ± 0.2 × 10 ¹⁷	61–69
4	O ₂	10	300	4.2 ± 0.2 × 10 ¹⁷	90–100
2	O ₂	8	300	0.6 ± 0.06 × 10 ¹⁷	13–17
2	O ₂ +He	9	300	0.6 ± 0.06 × 10 ¹⁷	13–17
2	O ₂ +N ₂	8	300	3.0 ± 0.1 × 10 ¹⁷	84–90
2	O ₂ +H ₂	8	300	2.9 ± 0.1 × 10 ¹⁷	80–85
4	O ₂	10	300	4.2 ± 0.2 × 10 ¹⁷	90–100
4	O ₂ +H ₂	10	300	5.5 ± 0.9 × 10 ¹⁷	102–148
4	O ₂	20	300	6.0 ± 0.6 × 10 ¹⁷	60–74
4	O ₂ +H ₂	20	300	8.8 ± 1.0 × 10 ¹⁷	88–116
4	O ₂	50	300	11.0 ± 2.0 × 10 ¹⁷	41–60
4	O ₂ +H ₂	50	300	14.1 ± 2.2 × 10 ¹⁷	55–75
4	O ₂ +air	50	300	12.3 ± 1.8 × 10 ¹⁷	51–62

absorption cross section vary widely as mentioned earlier. Uncertainties in the relative intensity ratios of the lines from the atomic oxygen lamp will also effect the calculated flux, but not to such a large extent. For these reasons we have tried to calibrate the AA measurement with a silver-coated quartz crystal rate monitor (silver-QCM) measurement.^{17,18} The key to the silver-QCM measurement is the ability of atomic oxygen to diffuse into silver at room temperature leading to mass accumulation and, hence, a detectable frequency change for the oscillator. A silver-QCM measurement of our ECR source with an input of 10 sccm of molecular oxygen and a power of 100 W showed a frequency change of 8.46×10^{-2} Hz/s, indicating a flux of 3.5×10^{15} atoms/cm² s. No absorption was detected with the AA. This may be expected as the calculated minimum detectable flux for the AA is 1.1×10^{16} atoms/cm² s at present. Measurements of the FTMP source in a range of $4 \times 10^{16} - 1 \times 10^{18}$ atoms/cm² s, as measured by the AA, all showed a silver-QCM measured flux of $\sim 5 \times 10^{15}$ atoms/cm² s. This suggests there is a limiting step in the oxidation of silver by atomic oxygen at room temperature making the silver-QCM measurement inappropriate for fluxes greater than $\sim 5 \times 10^{15}$ atoms/cm² s, and thus not allowing a good calibration check for the AA detection scheme at this time.

In summary, while maintaining chamber pressures compatible with molecular beam epitaxy-like thin-film growth of oxides and minimizing the production of energetic ionized oxygen we generate, and noninvasively detected $\approx 1.0 \times 10^{18}$ atoms/cm² s of atomic oxygen consistently over a series of months. This flux is about two orders of magnitude larger than the largest flux previously published for an atomic oxygen source. The largest effect on the generation of atomic oxygen with our flow-through microwave plasma source was the addition of H₂ or air ($\ll 1$ sccm) to the O₂ and the use of the boric acid surface treatment for the quartz confinement tube. Calculation of the dissociation efficiency of this source suggests that the nondestructive real-time atomic absorption detection scheme, while very good for

relative measurements, requires better knowledge of the cross section and lamp profile to be a good absolute measure of atomic oxygen. We also found the use of a silver-coated quartz crystal monitor to measure the atomic oxygen flux to be unsuitable for fluxes greater than $\sim 5 \times 10^{15}$ atoms/cm² s.

This work was supported by the NSF through the Stanford MRSEC program, and by the Air Force Office of Scientific Research.

- ¹K. Torii, F. Yano, and Y. Fujisaki, *J. Mater. Res.* **13**, 1015 (1998).
- ²A. Sawa, H. Obara, and S. Kosaka, *Appl. Phys. Lett.* **64**, 649 (1994).
- ³A. Tsukamoto, J. G. Wen, K. Nakanishi, and K. Tanabe, *Physica C* **292**, 17 (1997).
- ⁴M. Kanai, K. Horiuchi, T. Kawai, and S. Kawai, *Appl. Phys. Lett.* **57**, 2716 (1990).
- ⁵M. Ogihara, H. Abe, and T. Yamada, *Jpn. J. Appl. Phys., Part 2* **30**, L793 (1991).
- ⁶K. Yamamoto, R. H. Hammond, and J. S. Harris, Jr., *J. Vac. Sci. Technol. A* **9**, 2587 (1991).
- ⁷J. P. Locquet and E. Machler, *J. Vac. Sci. Technol. A* **10**, 3100 (1992).
- ⁸D. M. Lind, S. D. Berry, G. Chern, G. Mathias, and L. R. Testard, *Phys. Rev. B* **45**, 1838 (1992).
- ⁹T. Hashimoto, H. Koinuma, and K. Kishio, *Jpn. J. Appl. Phys., Part 1* **30**, 1685 (1991).
- ¹⁰ $n_j = n_o [(2j+1) \exp(-E_j/kT)] / [\sum_j (2j+1) \exp(-E_j/kT)]$, where n_j is the number density of O(²P_j) atoms and n_o is the total number density of atomic oxygen. See, for example, K. Kita, T. Imamura, N. Iwagami, W. H. Morrow, and T. Ogawa, *Ann. Geophys. (Germany)* **14**, 227 (1996).
- ¹¹W. L. Wiese, M. W. Smith, and B. M. Glennon, *Atomic Transition Probabilities* (National Standard Reference Data Systems, National Bureau of Standards), Vol. 1.
- ¹²W. T. Rawlins and F. Kaufman, *J. Quant. Spectrosc. Radiat. Transf.* **18**, 561 (1977).
- ¹³C. L. Lin, D. A. Parkes, and F. Kaufman, *J. Chem. Phys.* **53**, 3896 (1970).
- ¹⁴Y. Matsuura and M. Miyagi, *Opt. Lett.* **23**, 1226 (1998).
- ¹⁵The dissociation efficiency is calculated as $\Gamma_{AO}/2\Gamma_{MO}$, where Γ_{AO} is the flux of atomic oxygen calculated from the AA measurement and Γ_{MO} is the flux of molecular oxygen entering the FTMP source calculated from the flow monitor.
- ¹⁶L. S. Yu-Jahnes, W. T. Brogan, A. C. Anderson, and M. J. Cima, *Rev. Sci. Instrum.* **63**, 4149 (1992).
- ¹⁷V. Matijasevic, E. L. Garwin, and R. H. Hammond, *Rev. Sci. Instrum.* **61**, 1747 (1990).
- ¹⁸H. Kinoshita, J. Ikeda, M. Tagawa, M. Umeno, and N. Ohmae, *Rev. Sci. Instrum.* **69**, 2273 (1998).