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of a Quartz Crystal Microbalance**

by

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THE LASER ABLATION OF GOLD FILMS AT THE ELECTRODE SURFACE OF A QUARTZ CRYSTAL MICROBALANCE

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ABSTRACT

We report in this letter the amount of gold removed by ablation with a pulsed laser operating at 532 and 355 nm, by using a quartz crystal microbalance as a mass detector. The results indicate that for the 532 and 355 nm pulsed laser ablation of gold thin films, 10^{13} - 10^{16} atoms per pulse are removed over the fluence range of 0.5-5.0 J/cm². The amount of ablated material is found to depend on the fluence at constant wavelength, and on the wavelength at constant fluence. In addition, the mass sensitivity distribution across the quartz crystal microbalance electrode has been characterized by using the laser ablation technique.

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THE LASER ABLATION OF GOLD FILMS AT THE ELECTRODE SURFACE OF A QUARTZ CRYSTAL MICROBALANCE

Pulsed laser ablation is a practical method for liberating molecules from the solid to the gas phase, and is currently employed in a variety of material science applications. These include: Sample analysis[1], thin film deposition[2], and the generation of reactive intermediates[3]. The mechanism of laser ablation has been investigated by surface analysis of the target before and after irradiation[4,5], spectroscopic studies of the ablation plume[6,7,8] and characterization of the deposited films[9,10,11]. In spite of the widespread usage and investigation of the laser ablation technique, many of the physical characteristics of the process remain ill-defined.

The amount of material removed in a laser ablation experiment can be measured with a quartz crystal microbalance[12]. The quartz crystal microbalance (QCM) is a piezoelectric device that consists of a quartz wafer fixed between two electrodes, which allows mass measurements in the nanogram level. This mass sensitivity arises from the dependence of the oscillating frequency on the total mass of the crystal, its electrodes, and any materials at the electrode surface. The mass changes at the QCM electrode surface are typically determined by the Sauerbrey equation[13] but for heavily loaded crystals, the Lu and Lewis equation, which takes into account the elastic properties of the deposited material, is better suited[14]:

$$m_f = \left(\frac{\rho_q v_q}{2\pi Z f_c} \right) \tan^{-1} \left(Z \tan \left[\frac{\pi(f_c - f_q)}{f_q} \right] \right) \quad (1)$$

where; m_f = the mass per unit area of the removed film; Z = the acoustic impedance ratio; f_q = frequency of the oscillator; f_c = frequency of the oscillator + film; ρ_q = density of quartz; v_q = shear wave velocity.

Materials deposited on the electrode of a QCM may be laser ablated and the induced frequency change is a direct measure of the amount of material removed. By ablating materials at the electrode surface of a QCM, the amount of material vaporized per laser pulse may be determined as a function of different characteristics of the incident laser beam, such as wavelength and fluence. The purpose of this letter is to describe our first studies using this experimental system, and to demonstrate the potential of this technique as a means of correlating the properties of lasers used routinely for ablation with the physics and chemistry occurring at the target surface. We report here the results of the 355 and 532 nm laser ablation of thin gold films at the electrode surface of a quartz crystal microbalance.

The apparatus consists of a 5 MHz AT-cut quartz crystal microbalance (Valpey-Fisher, Hopkinton, MA), supported by a nylon holder with copper contacts for the oscillator circuit. The entire QCM assembly is fixed at the center of a stainless steel vacuum cell with four arms (used for laser ports, oscillator circuit and vacuum throughputs) oriented at 90° angles to each other. The oscillator circuit was designed and constructed to drive the crystal at its resonant 5 MHz frequency, which is

monitored with a frequency counter (Hewlett Packard model HP 5384 A). Ablation was initiated by a Nd:YAG laser (Continuum YG581C; pulsewidth ~ 10 ns) operating on either the second (532 nm) or third (355 nm) harmonic at a repetition rate of 2 Hz. Laser exposure to the QCM was controlled via a manual shutter. The laser beam was focussed onto the electrode surface of the QCM with a 150 mm f.l. lens. Fluence values were varied by keeping the laser spot size constant while incrementing the unfocussed laser power from 1 mJ/pulse to 10 mJ/pulse (measured by a calibrated Scientech laser power meter, model 372), at both wavelengths. The laser spot size was between 0.5 mm and 1.0 mm in diameter. Ablation was performed on heavily coated electrodes (3000-5000 Å) to minimize the probability of damaging the quartz crystal at higher fluences.

A typical experiment consists of performing single shot pulsed ablation at nine different positions on the electrode surface of the QCM and plotting the frequency history as a function of the number of laser pulses (*cf.* figure 1). The data were fit with a linear least squares routine and the slope of the fitted plot gives the average induced frequency change per pulse. The amount of material ablated per pulse is calculated by substituting the average frequency change into equation 1. This experiment is then repeated at various fluence values. Figure 2 shows our results for the pulsed laser ablation of gold over a range of fluence values at the wavelengths 532 and 355 nm. The data has been fit to a line by standard linear regression techniques, as shown in Figure 2. The threshold for ablation at both wavelengths is *ca.* 0.5 J/cm^2 , slightly lower than previous measurements made by the indirect

method of monitoring deposition of thin films[15].

For the experiments described above, the nine laser shots were positioned 0.35 mm from each other, forming a 3 x 3 grid. Increasing the number of shots at the electrode requires a larger electrode area on the microbalance, which compromises the sensitivity. The mass sensitivity of a QCM obeys a gaussian distribution, with the greatest mass sensitivity at the center of the electrode, which radially decays to zero as we move outward toward the edges of the electrode[14]. A second type of experiment was performed to verify the sensitivity of the QCM with respect to laser position on the electrode. In this case, the laser shots were positioned linearly across the entire electrode surface. Figure 3 shows a plot of the change in frequency as a function of the position of the laser on the QCM electrode fitted to a gaussian distribution. Since the reproducibility of the removal of material from shot to shot has been established near the center of the electrode (see figure 1), the plot in figure 3 represents the change in mass sensitivity observed across the QCM electrode. This sensitivity profile, mapped by the laser ablation technique, agrees with results reported elsewhere by using other methods[16,17]. The 3 x 3 grid (*cf.* figure 1) used for measuring the amount of material ablated was always contained within a distance of ± 1 mm from the absolute center of the QCM.

Table 1 summarizes our data for gold ablation obtained with the QCM. The table also includes for comparison, the data of Kelly, *et al.*, who used scanning electron microscopy to monitor gold surfaces following excimer laser ablation at 193 nm[4]. By measuring the volume of the ablated crater, they were able to estimate the average

amount of material vaporized per pulse (see Table I). At different wavelengths, it can be seen that from the table that 355 nm photons are more efficient at removing gold from the thin films than the other two wavelengths. Rebouillat, *et al.*, [15] have reported deposition rates of gold, copper and aluminum thin films following laser ablation at 355 and 532 nm. They found higher rates of deposition for 355 nm ablation of gold than for 532 nm, in agreement with our results here. Rebouillat, *et al.* indicate that their results can be explained on the basis of thermal effects in the material. Recent results, obtained by using this technique in our laboratory, suggest that other factors, *e.g.* optical properties of the thin film, may play an important role[18].

Direct comparisons between the excimer laser results of reference 4 and our Nd:YAG laser results, or with those of Rebouillat, *et al.* [15], must be viewed with caution. The observations may be the result of the differences between the optical characteristics of Nd:YAG laser vs. excimer laser, *e.g.* pulse duration, beam homogeneity, and frequency bandwidth, or it may be indicative of different physical processes occurring in the material. These phenomena are best studied by direct comparisons of pulsed laser ablation under conditions where the beam characteristics of the laser are kept constant.

Most of the studies of laser ablation depend on the data collected after multiple laser pulses at the target surface. Direct probes of the laser ablation plumes are typically limited to the detection of either neutral species or ionic species, exclusively. The microbalance experiment directly yields the mass removed per pulse, which

includes all neutral and ionic species (less any re-deposited material[19]) on the QCM electrode. The results presented here provide evidence that the microbalance pulsed ablation technique holds promise for the establishment of direct relationships among laser parameters and target characteristics in the laser ablation of refractory metals. Target properties such as reflectance, thermal conductivity and heat capacity, among others, have been reported to play an important role in the laser ablation process[4,5]. Ongoing experiments in our laboratory to: (1) Investigate other refractory metals, e.g. copper and aluminum; (2) Perform more thorough wavelength and fluence dependence studies; and (3) Study the effects of laser pulsewidth and beam homogeneity, will help establish the relationship between laser and target properties[18]. These results will provide a better understanding of laser ablation of metallic thin films.

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loans.

References

1. See for example, S.G. Hansen, *J. Appl. Phys.* **66**, (1989) 1411.
2. See for example, D. Dijkkamp, T. Venkatesan, X.D. Wu, S.A. Shaheen, N. Jisrawi, Y.H. Min Lee, W.L. Mc Lean and M. Croft, *Appl. Phys. Lett.* **51**, (1987) 619.
3. See for example, A.P. Salzberg, D.I. Santiago, F. Asmar, D.N. Sandoval and B.R. Weiner, *Chem. Phys. Lett.* **180**, (1991) 161.
4. R. Kelly, J.J. Cuomo, P.A. Leary, J.E. Rothenberg, B.E. Braren and C.F. Aliotta, in *Nuclear Instruments and Methods in Physics Research*, **B9**, Elsevier Science Publishers: North-Holland, Amsterdam, 1985, pp.329-40.
5. See for example, F. Heinrich and O. Bostanjoglo, *Appl. Surf. Sci.*, **54** (1992) 244
6. D.R. Olander, *Pure Appl. Chem.* **62**, (1990) 123.
7. H. Wang, A.P. Salzberg and B.R. Weiner, *Appl. Phys. Lett.* **59**, (1991) 935.
8. P.D. Gupta and S.R. Kumbhare, *J. Appl. Phys.* **55**, (1984) 120.
9. M. G. Karkut, M. Guilloux-Viry, A. Perrin, J. Padiou and M. Sergent, *Physica C (Amsterdam)* **179**, (1991) 262.
10. S. Airhaghi, A. Archer, B. Taguiang, R. McMin, P. Barnes, S. Tarling and I.W. Boyd, *Appl. Surf. Sci.* **54** (1992) 205.
11. A. Cross, H. Dallaporta, S. Lazare, H. Hiraoka, N. Merk and W. Marine, *Appl. Surf Sci.* **54** (1992) 278.
12. S. Lazare and V. Granier, *J. Appl. Phys.* **63**, (1988) 2110.
13. G.Z. Sauerbrey, *Z. Phys.* **155**, (1959) 206.
14. C. Lu in *Methods and Phenomena 7; Applications of Piezoelectric Quartz Crystal Microbalance*, eds. C. Lu and A.W. Czanderna, Elsevier Science Publishing: New York, 1984, pp. 19-61.
15. J.P. Rebouillat, B. Michelutti, Y. Souche, J.P. Gavigan, D. Givord and A. Lienard, in *Mater. Res. Soc. Symp. Proc.*, **151**, (Growth, Charact. Prop. Ultrathin Magn. Films Multilayers), eds. B.T. Jonker, J.P. Heromans and E.E. Marinero, Materials Research Society, 1989, 259-64.

16. P.J. Cumpson and M.P. Seah, *Meas. Sci. Technol.* **1**, (1990) 544.
17. M.D. Ward and E.J. Delawski, *Anal. Chem.* **63**, (1991) 886.
18. J. Pérez, B. Reyes and B.R. Weiner, *to be published*.
19. We believe that the amount of re-deposited material is $\leq 20\%$ based on the shape of the laser ablation plume observed, and estimates made in other studies.[16,17]
20. M.A. Cappelli, P.H. Paul, and R.K. Hanson, *Appl. Phys. Lett.* **56**, (1990) 1715.
21. G. Chen and E.S. Yeung, *Anal. Chem.* **60**, (1988) 864.

Figure Captions

Figure 1: The measured changes in frequency per laser pulse for the laser ablation of gold at 532 nm and a fluence of 2.5 J/cm^2 . The average amount of gold ablated per pulse is given by the slope of the fitted line, i.e 202 Hz/pulse (1162 ng/pulse).

Figure 2: The amount of gold ablated as a function of laser fluence for the laser ablation of gold at 532 and 355 nm. The error bars correspond to shot-to-shot variations in the laser fluence. The lines are linear least square fits to the data.

Figure 3: The induced change in frequency at different positions from the center of the electrode of a QCM. The experiment was performed at a constant fluence of about 2.5 J/cm^2 pulse. The solid line is a Gaussian distribution fitted to the experimental data. The dotted lines indicate the 2.2 mm region where the ablation experiments were performed.

Fig 1.

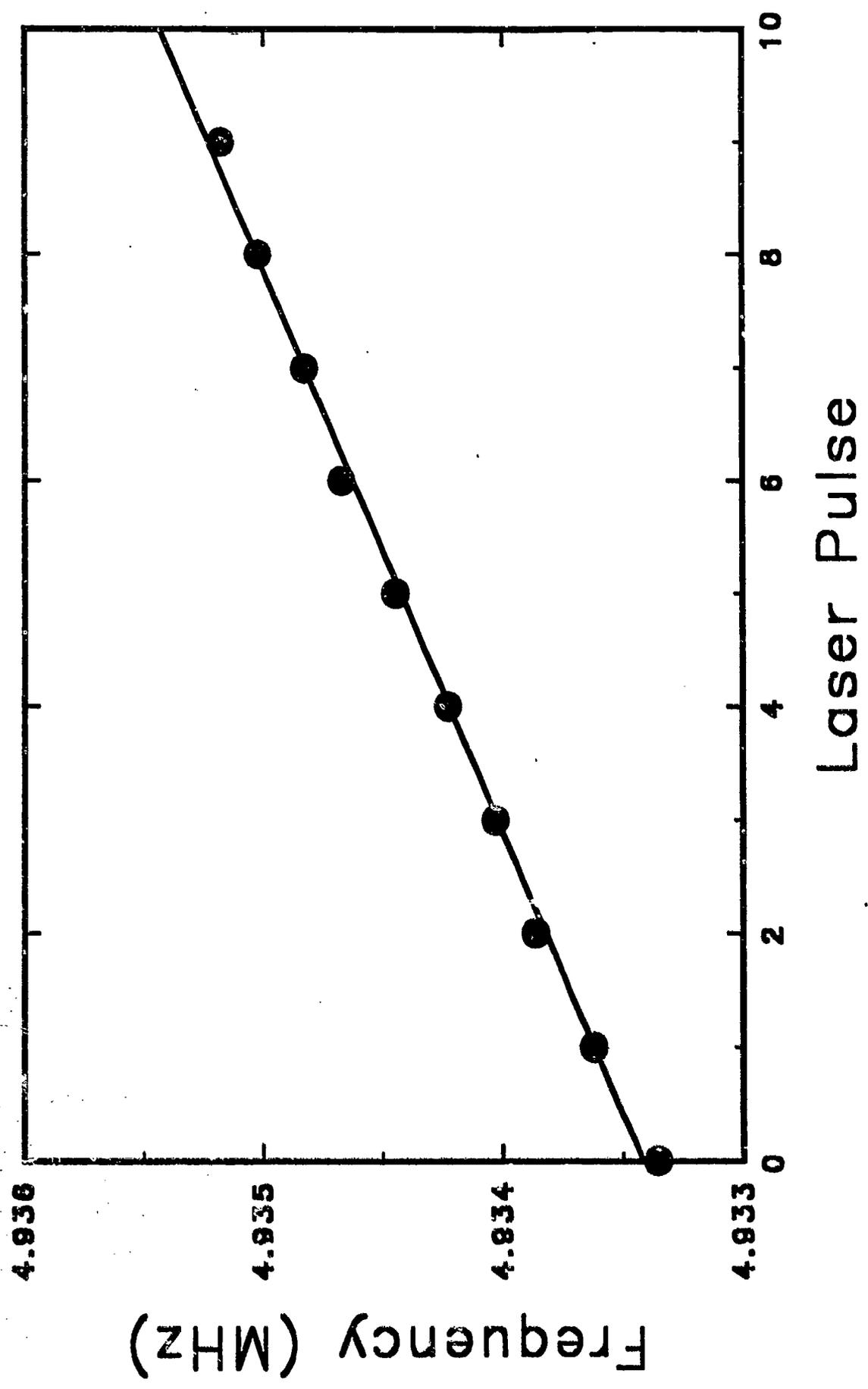


FIG 2

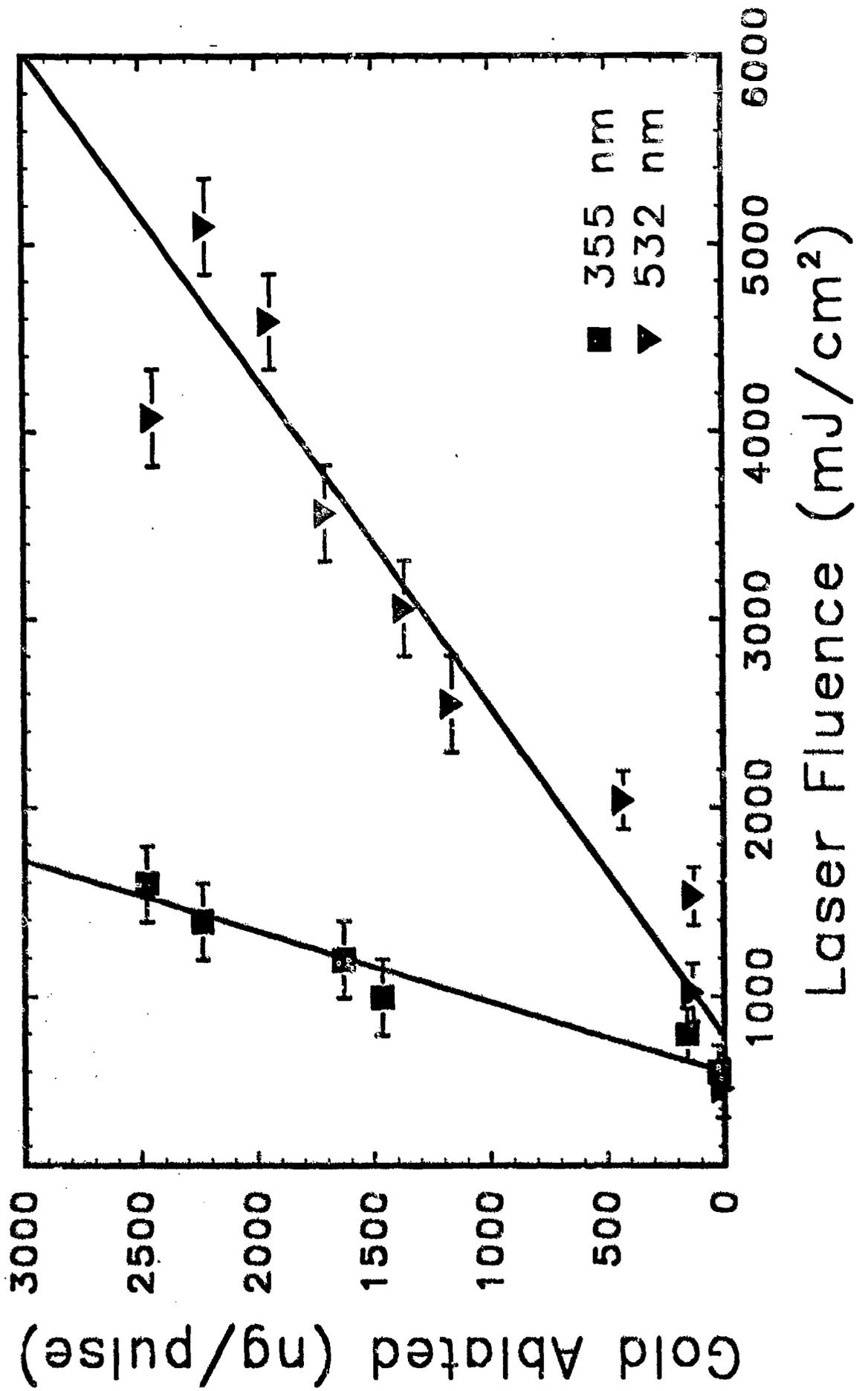


FIG. 3

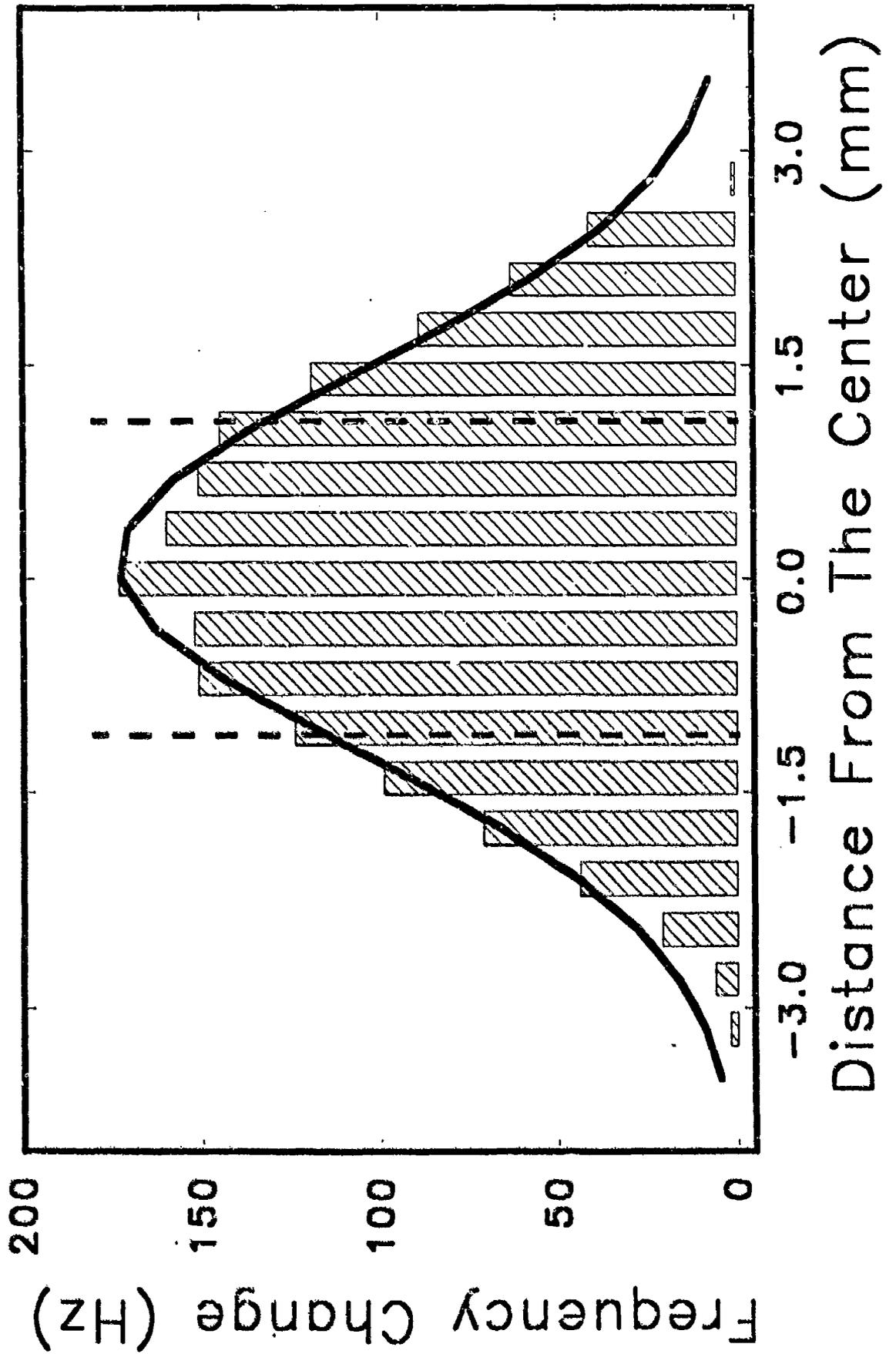


Table I. Results of 532 nm and 355 nm pulsed laser ablation of gold thin films. The results reported for excimer laser ablation at 193 nm were adapted from reference 4.

Wavelength (nm)	Fluence (mJ/cm ²)	Atoms Ablated per Pulse	Photon Density (photons/cm ²)	Photon Efficiency (atoms ablated/photon • cm ²)
532	509	1.72 X 10 ¹³	1.36 X 10 ¹⁸	1.26 X 10 ⁻⁵
	1019	4.13 X 10 ¹⁴	2.70 X 10 ¹⁸	1.51 X 10 ⁻⁴
	1528	3.95 X 10 ¹⁴	4.09 X 10 ¹⁸	9.66 X 10 ⁻⁵
	2037	1.31 X 10 ¹⁵	5.45 X 10 ¹⁸	2.40 X 10 ⁻⁴
	2546	3.55 X 10 ¹⁵	6.82 X 10 ¹⁸	5.21 X 10 ⁻⁴
	3056	4.17 X 10 ¹⁵	8.18 X 10 ¹⁸	5.10 X 10 ⁻⁴
	3565	5.21 X 10 ¹⁵	9.55 X 10 ¹⁸	5.46 X 10 ⁻⁴
	4074	7.48 X 10 ¹⁵	1.09 X 10 ¹⁹	6.86 X 10 ⁻⁴
	4585	5.93 X 10 ¹⁵	1.23 X 10 ¹⁹	4.82 X 10 ⁻⁴
	5093	6.77 X 10 ¹⁵	1.36 X 10 ¹⁹	4.98 X 10 ⁻⁴
355	597	7.12 X 10 ¹³	1.07 X 10 ¹⁸	6.65 X 10 ⁻⁵
	796	4.94 X 10 ¹⁴	1.42 X 10 ¹⁸	3.41 X 10 ⁻⁴
	995	4.84 X 10 ¹⁵	1.78 X 10 ¹⁸	2.52 X 10 ⁻³
	1194	4.98 X 10 ¹⁵	2.13 X 10 ¹⁸	2.34 X 10 ⁻³
	1393	6.84 X 10 ¹⁵	2.49 X 10 ¹⁸	2.75 X 10 ⁻³
193	1592	7.57 X 10 ¹⁵	2.85 X 10 ¹⁸	2.66 X 10 ⁻³
	2500	2.70 X 10 ¹⁶	2.43 X 10 ²¹	1.11 X 10 ⁻⁶