

Langmuir probe study of plasma expansion in femtosecond pulsed laser ablation of silver

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ABSTRACT

A time-resolving Langmuir probe has been used to study the plasma plumes produced by ablation of silver with 200 femtosecond laser pulses at fluences of 1–12 J cm⁻² at a central wavelength of 775 nm. Initial results have shown that surface contamination, and subsequent recontamination, can significantly influence the time of flight (TOF) signals obtained using the Langmuir probes. Surface conditioning techniques have been developed to overcome these influences. The TOF signals have been used to establish that the threshold fluence for the laser produced plasma in silver, under the present operating conditions, occurs at 1.04 J cm⁻². The angular dependence of the magnitude of the ion yields and energies, at the time when the ion flux is maximized, agree with the predictions of Anisimov's self-similar isentropic model of the plasma expansion.

Keywords: Laser ablation, femtosecond pulsed laser, laser induced plasma, Langmuir ion probe, time-of-flight metals.

1. INTRODUCTION

Ultrashort laser materials processing continues to receive a lot of attention mainly due to the major differences between the laser material interaction when processing with nanosecond and femtosecond laser pulses¹. Ultrashort laser pulses offer the advantages of minimal thermal damage to the target. The formation of plasma plumes occurs after the termination of the laser pulse and this prevents any plasma shielding effects.¹ Extensive studies of ultrashort laser ablation of metals below the threshold for plasma formation have been carried out and various laser material-interaction mechanisms have been proposed.^{2,3} However, less attention has been paid to ultrashort laser ablation of metals above the threshold for plasma formation, especially with regard to the ionic component of the ablation plumes.

Langmuir ion probes have been used extensively to investigate the plasma parameters of nanosecond laser produced ablation plumes from metal targets.⁴⁻⁶ More recently they have also been applied to ultrafast laser produced plasmas.^{7,8} Such Langmuir probes enable the ionic component of the ablation plume to be studied relatively easily. However, they provide no information on the neutral components of the ablation plume, the study of which requires more complicated methods, such as mass spectrometry.

Metal samples are normally covered with a thin layer of surface impurities. These surface layers consist of light atoms of hydrogen, carbon and oxygen.⁹ In Langmuir probe TOF experiments of heavy atomic targets the impurities appear as separate fast peaks before the true signal from the metal target. These impurities are removed by the first few laser pulses but it will be shown in this work that the surface becomes recontaminated after a number of seconds. It has been shown elsewhere that this recontamination is due to the impurities themselves and not the residual gas in the vacuum chamber.⁹

The behaviour of expanding laser produced plasma plumes has previously been explained using the self-similar, adiabatic model of plume expansion developed by Anisimov et al.^{10,11} Strictly, this model applies to the expansion of a

neutral gas but it has been shown previously⁴ that, with the correct choice of parameters, the model can be used to describe the dynamics of a laser ablation plasma.

2.0 EXPERIMENTAL

The ablation was performed using linearly polarized pulses of 200 fs duration from a commercially available Ti-sapphire laser (Clark MXR, CPA2001) at a central wavelength of 775 nm. A repetition rate of 10 Hz was used for all experiments. The experimental set-up used to control important parameters such as the beam energy, number of incident laser shots, etc., is described in detail in earlier work.¹² The laser pulses were focused with a 250 mm lens and were directed at normal incidence onto a silver target in a vacuum of 10^{-6} torr. The laser spot on the target had an area 2×10^{-5} cm² and was slightly elliptical ($b/a = 1.4$) with the minor axis, a , in the same plane as the diagram in Fig. 1. It has been shown previously that the ablation plume is marginally wider in the direction of the minor spot axis.^{10,11} The values of the laser fluence were varied between 1 and 12 J cm⁻², corresponding to laser intensities in the range of 6 - 60 TW cm⁻².

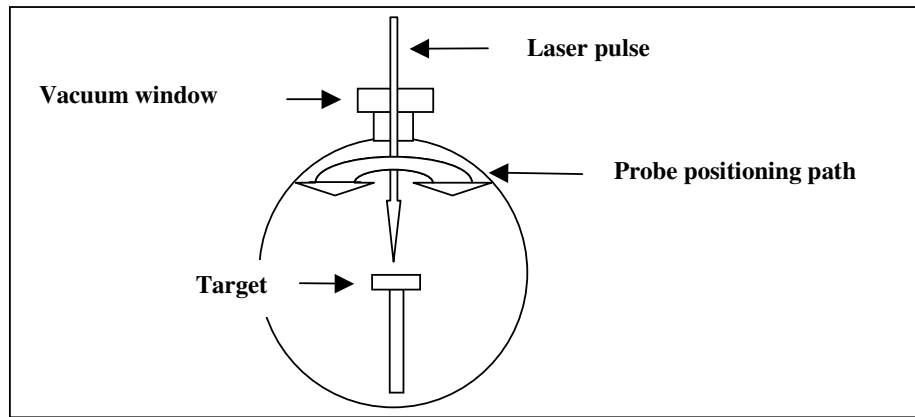


Fig. 1. The Langmuir probe experimental arrangement.

One Langmuir probe, positioned at distances between 2 cm and 5.4 cm from the target, was used in these experiments. The probe was orientated to face the irradiated spot on the target, i.e. perpendicular to the plasma propagation. The angular position of the probe could be varied in the plane of the diagram by adjusting a rotational feed-through axis, whilst the radial probe distance and probe-target orientation were kept fixed, see Fig. 1. All angles were measured relative to the target normal. The probe is the tip of a tin-soldered copper wire with a projected area of 0.011 cm² at the end of an insulated cable. During the experiments the probe is biased at -25 V and the collected ion current is determined by the voltage signal recorded across a load resistor on a digital oscilloscope. A fast photodiode is used to trigger the oscilloscope at the instant the laser irradiates the target. While a measurement is being made the silver target and the vacuum chamber are grounded.

3.0 RESULTS & DISCUSSION

Surface Contamination Effects

Initial experiments using the Langmuir probes dealt with the issue of surface impurities and their effect on the TOF signals. Experimental results show that, by taking a single acquisition signal from an untreated area on the target surface the TOF signal showed two distinct peaks. The first peak is fast and is due to the surface impurities,⁹ the second peak is slower and is associated with the actual target ions. The signals shown in Fig.2 illustrate this observation. The contaminant peak is prominent for the 1st laser shot on an untreated area of the target surface. It is less dominant when an average is taken of the signals from the first twenty laser shots on an untreated area of the target surface. In this case the signal for the target Ag ions dominate as can be seen in Fig. 2.

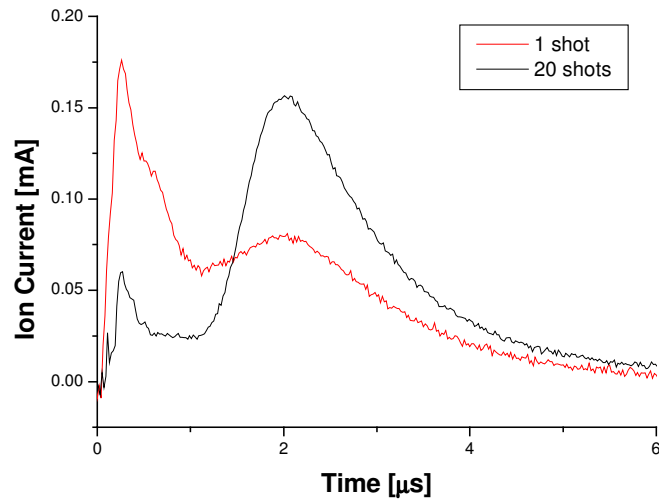


Fig. 2. Ion current signals collected at the langmuir probe following femtosecond laser irradiation of a silver target. The single shot signal shows a prominent fast peak due to surface impurities. Averaging over 20 acquisitions results in a less prominent fast peak and the signal due to the target ions dominates. The probe target distance was 2.5 cm and the bias voltage was -25 V.

Fig. 2 shows that the effect of the surface impurities on the TOF signal is less pronounced after a certain number of laser pulses. This is the result of surface cleaning by the initial laser pulses. To investigate this further, individual signals were generated from successive pulses at the same spot on the target surface. Signals were generated in this way for the 1st to the 20th shot and the results obtained are illustrated in Fig.3. They show that by the 17th pulse the surface was cleaned of impurities as the fast contaminant peak is completely absent.

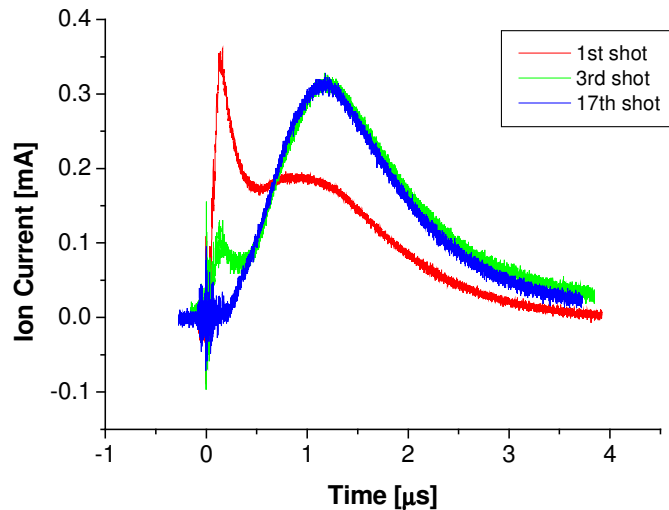


Fig. 3. Ion current signals collected at the langmuir probe following femtosecond laser irradiation of a silver target. The effect of surface cleaning is clearly evident as the contamination peak reduces from the 1st to the 3rd shot and is completely absent for the 17th shot. The probe target distance was 2.0 cm and the bias voltage was -25 V.

The results presented in Fig.3 indicate how many laser pulses are required to clean the surface of the silver target of impurities. However, they do not provide any information on the dynamics of the recontamination of the previously cleaned surfaces. Experiments have shown that the target surface becomes recontaminated after a certain amount of time. Signals acquired from previously cleaned areas of the target surface showed clear evidence of impurity ions in the

form of the fast peaks mentioned previously. The amount of time between cleaning and acquisition shots was varied and the results are presented in Fig. 4.

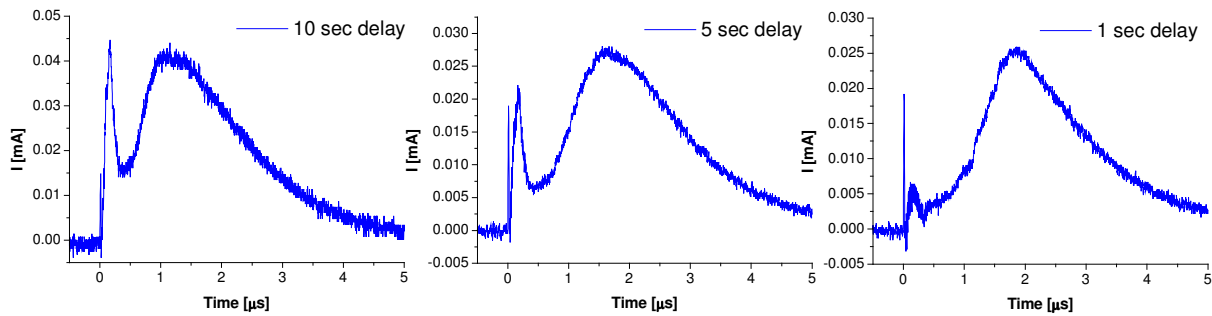


Fig. 4. Ion current signals collected at the langmuir probe following femtosecond laser irradiation of a silver target. The target was first irradiated with 100 laser shots. The laser was then turned off, and after a set delay a signal was acquired using a single laser shot. Note the reduction of the contamination peak as the delay is reduced. The sharp peaks at $t = 0$ are due to the photoelectric effect of the laser light on the probe. The probe target distance was 2.5 cm and the bias voltage was -25 V.

The results presented in Fig.4 show that after cleaning the target surface of impurities, recontamination occurs in a matter of seconds. Even with just one second between the cleaning and the acquisition shots we can see evidence of the surface becoming recontaminated. It is not clear why the main ion peak shifts towards longer times as the delay is reduced. These results show that to overcome the influence of surface contamination, and subsequent recontamination, the surface must be irradiated with a number of cleaning laser shots. Signals should then be acquired directly after cleaning to avoid any effects due to surface recontamination. For the TOF signals generated for the remainder this work the target was first irradiated with 50 cleaning laser shots and the signals were acquired by averaging over the next 16 shots. The number of cleaning shots used was increased to 50 (as opposed to 17) because it was found that the amplitude of the current signals reached a saturation value after the target had been irradiated with about 40 laser pulses.

Laser Induced Plasma Threshold Determination

In order to determine the threshold fluence for the onset of the laser produced plasma, TOF signals were obtained for a range of fluence values and the results are presented in Fig. 5. It is clear from Fig.5 that there is a reduction in the amplitude of the ion signals, and thus the amount of ions being removed, as the laser fluence is reduced. The total amount of charge per pulse, F , collected at the probe can be found by integrating over the ion current signals. (This quantity also represents the number of ions arriving at the probe perpendicular to the plasma flow direction, provided all of the ions are singly charged). A total of ten TOF ion current signals (each of which was an average of 16 signals) were generated for each value of laser fluence. In this way, average and statistical error values for F were obtained. Fig. 6 shows a plot of these F values versus laser fluence. The behaviour of the data suggests that a linear relationship exists between the total charge removed per pulse, F , and the laser fluence, ϕ . By extrapolation to $F = 0$, it is possible to determine that the threshold fluence for the onset of the laser produced plasma occurs at $\phi = 1.04 \text{ J cm}^{-2}$. Elsewhere⁸ it has been reported that for gold a logarithmic relationship exists between the ion yield and the laser fluence, but the best fit to our data was for a linear relationship.

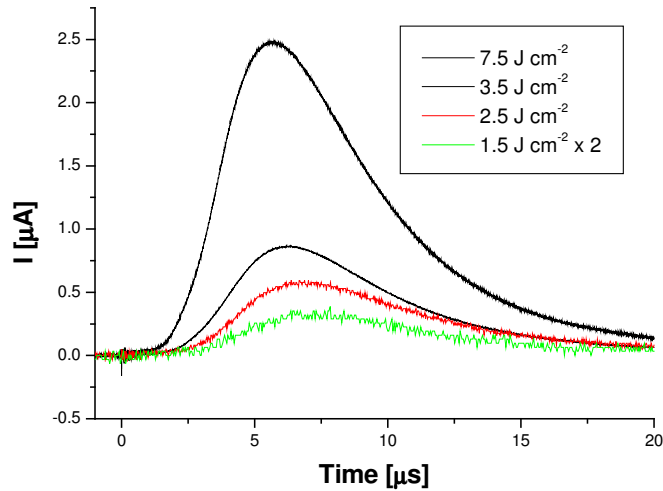


Fig. 5. Ion current signals collected at the langmuir probe following femtosecond laser irradiation of a silver target at the fluence values shown. The probe target distance was 5.4 cm and the bias voltage was -25 V.

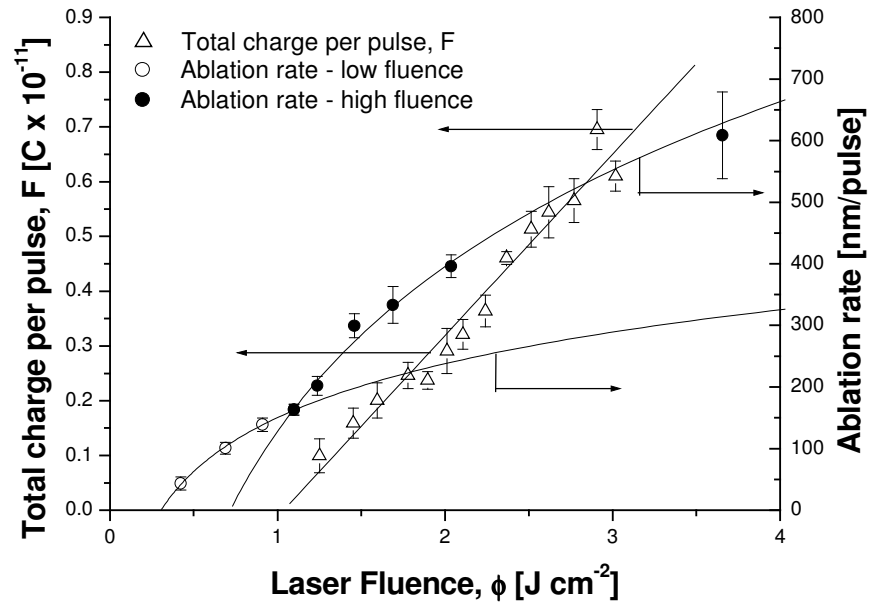


Fig. 6. The total amount of charge per pulse, F , collected at the probe versus the applied laser fluence, ϕ . Each data point has been obtained by integrating a TOF distribution, as shown in Fig. 5. By extrapolation to $F = 0$ the threshold fluence for the onset of the laser produced plasma is found to be at $\phi = 1.04$ J cm^{-2} . Also plotted is the ablation rate of silver in terms of the depth removed per pulse. Note that the threshold for plasma formation coincides with the increase in the ablation rate.

Also shown in Fig. 6 is the ablation rate of silver in terms of the depth removed per pulse. In earlier work,¹² we have shown that there are two distinct ablation regimes in ultrafast laser processing of metals. The ablation rate is proportional to the logarithm of the applied fluence and there is a sharp rise in the rate at a given fluence value which has been explained in terms of the two temperature model.¹³ It should be noted that the first ablation regime (low fluence) does not occur for nanosecond laser pulses. Interestingly, we have found that the threshold for the onset of the laser produced plasma occurs at roughly the same value of laser fluence where the transition between the two ablation

regimes occurs ($\phi = 1.24 \text{ J cm}^{-2}$). A similar trend was observed for stainless steel. This might suggest that the low fluence regime in femtosecond laser ablation of metals occurs without significant plasma formation. Various material removal mechanisms have been proposed for femtosecond laser ablation below the threshold for plasma formation,³ which may account for the ablation phenomena in the low fluence regime.

Inspection of the TOF signals presented in Fig.5 can reveal information on the ion velocities. Elsewhere^{7,8} it has been reported that two distinct peaks have been observed during TOF investigations of femtosecond laser ablation of metals. These peaks are said to correspond to fast and slow ions produced by femtosecond laser ablation. This has not been observed in this work, perhaps because of insufficient distance between the probe and the target. The time value at the onset of the signal, t_{onset} , can be used to calculate the velocities of the fastest components at the leading edge of the plasma plume. In the same way, the peak flight time, t_m , can be used to calculate the velocities of the ions at the peak signal, or the mean velocity.

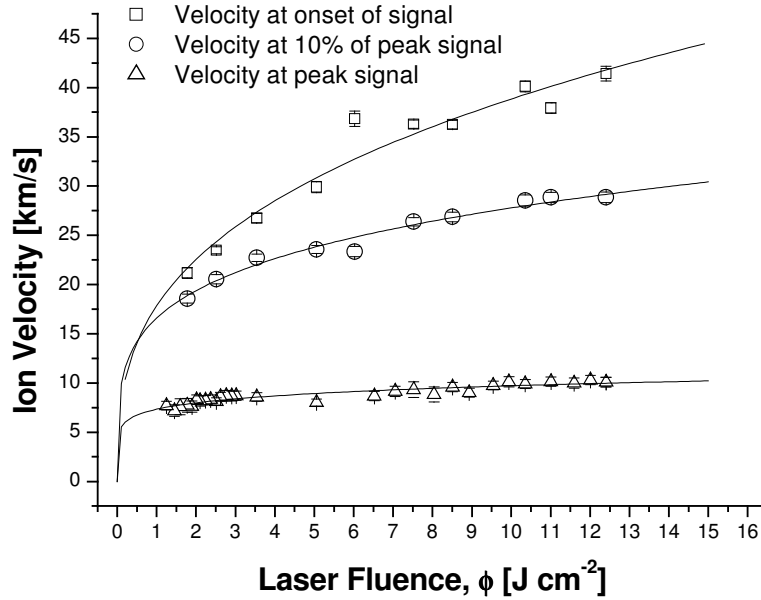


Fig. 7. The ionic velocities calculated for different velocity distributions in the TOF signals plotted against the laser fluence. The solid lines represent fits to a power law dependence. The components which arrived at the time corresponding to 10% of the peak ion signal comprise roughly 1% of total ion yield.

Elsewhere,¹⁵ it has been reported that the ion velocity is proportional to the square root of the applied fluence ($v \propto \phi^{0.5}$). This analysis was based on the assumption that a proportion of the laser energy deposited into the material was converted into the kinetic energy of the ions and hence the square root dependence. Our results show a power law dependence but the exponent is always less than 0.5 (0.34 for the onset velocities and 0.12 for the velocity of the ions at the peak signal). Fig. 7 shows that the mean velocities range between 6-10 km/s, with a weak dependence on the applied laser fluence. These velocities correspond to ion energies in the range of 30-60 eV. However, the velocities of the fastest components in the plasma range between 20-45 km/s with corresponding ion energies in the range of 0.25 -1.0 keV. Thus, we can conclude that the ion velocity increases with laser fluence, but the rate of increase is much more pronounced for the faster plume components.

Angular Variation of ion density and energy

In order to investigate the angular variation of the ion yield and energy, TOF signals were obtained for a range of angular values at a fixed fluence value of $\phi = 5 \text{ J cm}^{-2}$ and at a radial distance of 5.4 cm. Fig. 8 shows the variation of the ion TOF signals for the angular values shown.

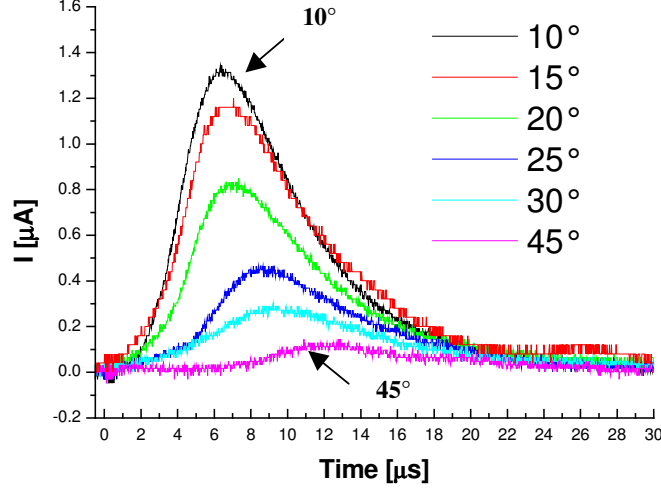


Fig. 8. Angular variation of the ion signals at 5 J cm^{-2} . The probe target distance was 5.4 cm and the bias voltage was -25 V .

Fig. 8 shows that both the signal amplitudes and the ion velocities are strongly peaked towards the target normal. This behaviour is consistent with the plasma expansion model of Anisimov et al.^{10,11} The model does not deal with the processes leading to the formation of the plasma. It describes its expansion from an initial condition at the end of the laser pulse where the plasma exists as a thin ellipsoidal layer on the target surface, with maximum dimensions $2X_0$, $2Y_0$ and Z_0 . X_0 and Y_0 are the semi-major and semi-minor radii of the initial plume and Z_0 is the initial plume thickness perpendicular to the target. In the model the plume expands such that temperature, density and entropy are constant on ellipsoidal surfaces. According to the model the plasma volume grows as t^3 , once the initial acceleration is complete. This occurs when the plasma has expanded a few mm along the target normal.⁴ The ion current onto a probe is given by

$$I = n_i A v, \quad (1)$$

Where n_i is the number of ions per unit volume or the ion density, A is the probe area and $v = R/t$ is the ion velocity, where R is the radial coordinate of the probe. Thus the model predicts that, as the angle of detection is varied, the maximum value of the ion current will vary as $1/t_m^4$, where t_m is the TOF at the maximum ion signal. Fig. 9 shows the angular variation of the measured values for the maximum ion current. Using the measured values of t_m , from Fig. 8, the $1/t_m^4$ scaling suggested by the Anisimov model is calculated and included in the plot. The close agreement of the two plots show that the ion signals in Fig. 8 do approximately follow the $1/t_m^4$ scaling, thus good temporal agreement is displayed between the model and the experimental results for femtosecond laser produced plasma expansion.

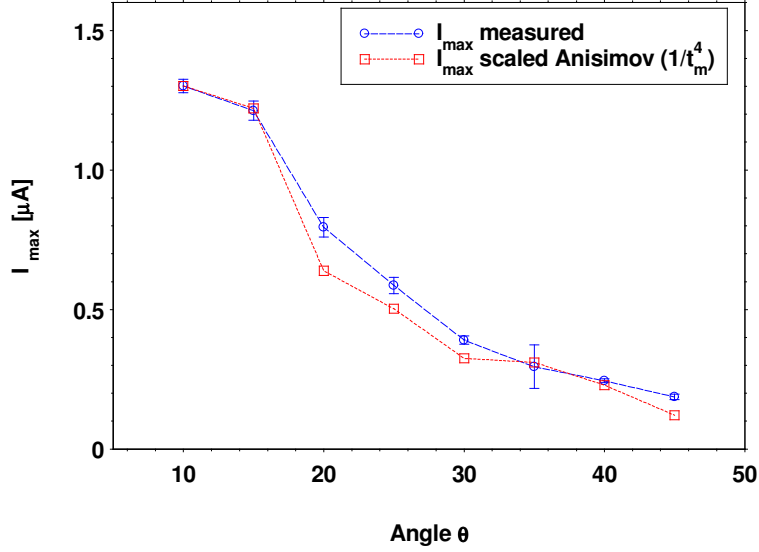


Fig. 9. Angular variation of the measured values of the amplitude of the maximum ion flux at 5 J cm^{-2} . The maximum ion flux is compared to the data generated by the $1/t_m^4$ scaling suggested by the Anisimov model. The two curves have been normalised at 10° .

According to the expansion model the angular distribution of ions in the plume at expansion times on the order of microseconds is given by^{10,11}

$$\frac{F(\theta)}{F(0)} = (1 + \tan^2 \theta)^{3/2} \left[1 + \left(\frac{Z_{\text{inf}}}{X_{\text{inf}}} \right)^2 \tan^2 \theta \right]^{-3/2}, \quad (2)$$

where $Z_{\text{inf}}/X_{\text{inf}}$ is the ratio of the limiting value of the cloud front along the Z-axis (directed along the target normal) and the value of the front along the X-axis (parallel to the target surface). This quantity is known as the expansion ratio and it is a measure of the forward peaking of the plasma plume. By integrating the TOF signals in Fig. 8 the angular distribution of ions in the plume was determined. For practical reasons, as described in ref. 6, a Gaussian fit has been used to determine the value of $F(0)$, i.e. the ion yield along the target normal. All measured values have been normalised according to this value and the results are plotted in Fig.10. Fitting equation 2 to the data leads to a value for the expansion ratio of, $Z_{\text{inf}}/X_{\text{inf}} = 2.2 \pm 0.1$ (the uncertainty in the value arises from the degree of uncertainty associated with the fitting procedure). This is very close to the value measured by T. N. Hansen et al⁴ for ns laser ablation of silver at 355 nm. The close agreement between the measured data and the equation show that the expansion of the femtosecond laser produced plasma, in terms of the spatial distribution of the ions, is well described by the Anisimov model.

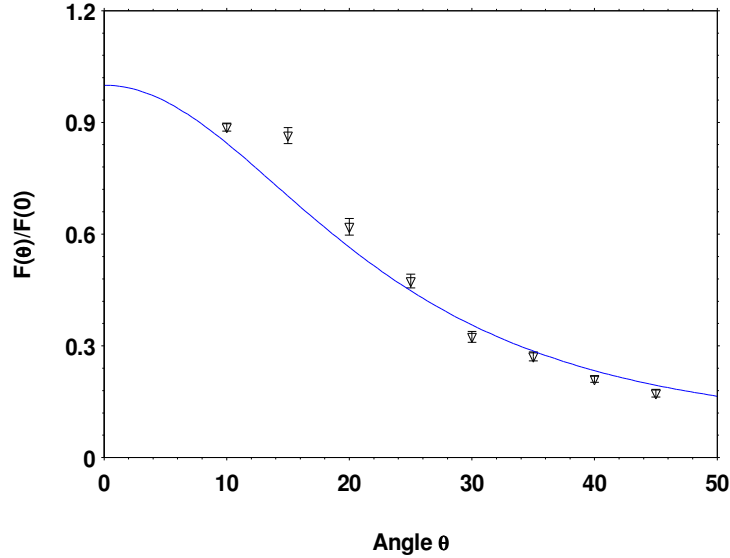


Fig. 10. Angular variation of the normalised ion yield at 5 J cm^{-2} . Each data point has been obtained by integrating a TOF distribution, as shown in Fig. 8. The line is a fit of equation (2) from Anisimov's model, where a Gaussian fit was initially used to estimate the ion yield at 0° .

4.0 CONCLUSIONS

We have used a Langmuir probe to study the plasma plumes produced by ablation of silver with 200 femtosecond laser pulses at fluences of $1\text{--}12 \text{ J cm}^{-2}$ at a central wavelength of 775 nm. The effects of surface contamination on the TOF signals have been demonstrated. We have shown that the surface impurities are removed by initial laser pulses, but that after a certain amount of time the surface becomes recontaminated. The Langmuir probe has been used to establish that the threshold fluence for the onset of the laser produced plasma in silver, under the present operating conditions, occurs at 1.04 J cm^{-2} . This value corresponds to the transition region between the low and high fluence regimes in the ablation rate of silver, which has been measured here ($\sim 1.24 \text{ J cm}^{-2}$), and is described by the two-temperature model.¹³ This result suggests that the low fluence regime in the femtosecond laser ablation of metals proceeds without significant plasma formation. The TOF signals have been used to study the dependence of the ion velocities on the applied laser fluence. The fastest plume components have velocities in the range of 20 – 45 km/s depending on the applied laser fluence, with corresponding energies in the range of 0.25-1.0 keV. The majority of ions in the plume travel with velocities between 6-10 km/s depending on the applied laser fluence. These velocities correspond to ion energies in the range of 30-60 eV. The dependence of the ion velocity and energy on the applied fluence is stronger for the fastest plume components. The temporal and angular dependence of the magnitude of the ion yields, at a fixed fluence value of 5 J cm^{-2} and at the time when the ion flux is maximized, agree with the predictions of Anisimov's self-similar isentropic model of the plasma expansion. The measured expansion coefficient, $Z_{\text{inf}}/X_{\text{inf}}$, of 2.2 is in good agreement with the value measured by T. N. Hansen et al⁴ for ns laser ablation of silver at 355 nm.

ACKNOWLEDGEMENTS

This work was supported by the Higher Education Authority Programme for Research in Third-Level Institutions (1999) and by the Enterprise Ireland Advanced Technology Research Programme (2000). Postgraduate student support is also acknowledged from the NUI-Galway Science Faculty Fellowship Programme and from the Enterprise Ireland Postgraduate Fellowship scheme.

REFERENCES

1. B.N. Chichkov, C. Momma and S. Nolte, "Femtosecond, picosecond and nanosecond laser ablation of solids", *Appl. Phys. A*, **63**, pp 134-142, 1996.
2. A. Cavalleri, K. Sokolowski-Tinten, D. von der Linde, "Femtosecond laser ablation of gallium arsenide investigated with time-of-flight mass spectroscopy", *Appl. Phys. Lett.* **72**, pp 2385, 1998.
3. D. S. Ivanov and L. V. Zhigilei, "Combined atomistic-continuum modeling of short pulse laser melting and disintegration of metal films", *Phys. Rev. B* **68**, pp 064114, 2003.
4. T. N. Hansen, B. Toftman, J. Schou, J.G. Lunney, "Langmuir probe study of plasma expansion in pulsed laser ablation", *Appl. Phys. A* **69** [Suppl.], pp 601, 1999.
5. B. Toftmann, J. Schou, T.N. Hansen, J.G. Lunney, "Evolution of the plasma parameters in the expanding ablation plume of silver", *Appl. Surface Science* **186**, pp 293-297, 2002.
6. B. Thestrup, B. Toftmann, J. Schou, B. Doggett, J.G. Lunney, "Ion dynamics in laser ablation plumes from selected metals at 355 nm", *Appl. Surface Science* **197-198**, pp 175-180, 2002.
7. S. Amoroso, X. Wang, C. Altucci, C. de Lisio, M. Armenante, R. Bruzzese, R. Velotta, "Thermal and nonthermal ion emission during high-fluence femtosecond laser ablation of metallic targets", *Appl. Phys. Lett.* **77**, pp 3728, 2000.
8. S. Amoroso, X. Wang, C. Altucci, C. de Lisio, M. Armenante, R. Bruzzese, N. Spinelli, R. Velotta, "Double-peak distribution of electron and ion emission profile during femtosecond laser ablation of metals", *Appl. Surface Science* **186**, pp 358-363, 2002.
9. D. Dinger, K. Rohr, H. Weber, "Dynamics of recontamination of laser cleaned metallic surfaces in laser produced plasma experiments", *J.Phys.D: Appl. Phys.* **17**, pp 1707-1712, 1984.
10. S.I. Anisimov, B.S. Luk'yanchuk, A. Luches, "An analytical model for three-dimensional laser plume expansion into vacuum in hydrodynamic regime", *Appl. Surface Science* **96-98**, pp 24-32, 1996.
11. S.I. Anisimov, D. Bäuerle, B.S. Luk'yanchuk, "Gas dynamics and film profiles in pulsed-laser deposition of materials", *Phys. Rev. B* **48**, pp12076, 1993.
12. P. Mannon, J. Magee, E. Coyne, G. M. O'Connor, T. J. Glynn, "The effect of damage accumulation behaviour on ablation thresholds and damage morphology in ultrafast laser micro-machining of common metals in air", *Appl. Surface Science*, **233**, pp 275-287, 2004.
13. S. Nolte, C. Momma, H. Jacobs, A. Tünnermann, B.N. Chichkov, B. Wellegehausen and H. Welling, "Ablation of metals by ultrashort laser pulses", *J. Opt. Soc. Am. B* **14**, pp 2716-2722, 1997.
14. V. Margetic, "Femtosecond laser ablation", PhD Thesis, University of Dortmund, 2002.