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Cw Ar^+ Laser-Induced Oxidation of Cu Layers

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Abstract. We investigate the early stages of oxidation of thin Cu films on glass substrates exposed to cw Ar^+ laser irradiation in air. We conclude that oxidation, which proceeds at rates up to μm/s, is due only to the heating effect of the laser beam and that, under our experimental conditions, the rate limiting step is a phase boundary reaction with $Q = 0.65$ eV.

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There have been a number of reports in the literature of laser-induced oxidation of metals by either pulsed or cw irradiation at wavelengths ranging from 196 nm to 10.6 μm. Clearly, exposure of an absorbing target to sufficiently intense laser radiation will induce a degree of heating which, in an oxygen containing atmosphere, may be sufficient to promote the formation of oxide layers. In a physical sense this may be described as "classical" oxidation, although it is worth noting that the use of a laser beam permits a control over spatial localization unattainable by other means and which may therefore be of great technological interest. There are cases, however, where the laser beam apparently does more than simply heat the target; either the oxidation rate is higher at a given induced temperature [1–3] or oxidation proceeds at temperatures normally insufficient [4–6] or in some cases the reaction products differ from those which result by heating the sample in another manner [7]. Various mechanisms have been proposed for this so-called laser-enhanced oxidation [8–10].

Thirdly, since the laser can give a degree of energy coupling into the sample surface greater than that which can generally be obtained by other means it might be possible to work in a previously unexplored oxidation regime where direct comparison with classical heating methods is difficult, or impossible.

We shall be concerned here mainly with the oxidation of thin Cu films on thermally insulating supports, exposed to cw Ar^+ laser irradiation in air. In these circumstances it is not difficult to achieve oxidation rates of μm/s, and we describe and discuss here a series of experiments designed to elucidate the oxidation mechanism(s) in this case.

1. Experimental

Our specimens are in the form of metallic films deposited onto glass substrates.

The ideal experiment for the determination of oxidation kinetics would be a non-destructive time resolved measurement of oxide thickness over a range of constant, and known, temperatures/irradiation conditions. In the case of laser-induced oxidation it would be advantageous to work with a beam spot of lateral dimension large compared to the thermal diffusion distance in the substrate, i.e. where a one-dimensional approximation is appropriate. Since, however, the maximum available Ar^+ laser output power does not allow this approach, the probe setup shown in Fig. 1 is used.

The primary Ar^+ beam is directed unfocussed to the specimen at incident beam powers up to ±12 W. Use of a broad-band reflector is necessary so that the precise spectral content of the primary beam is ill-defined though, particularly at higher powers, can be expected to include a large component at 514 nm. The beam profile was measured as near-Gaussian with a best fit 1/e power radius of 5×10^{-2} cm. An angled glass slide is used to pick off a portion of the primary beam which is attenuated and focussed down to ~50 μm dia at the specimen surface at the centre of the primary beam spot.

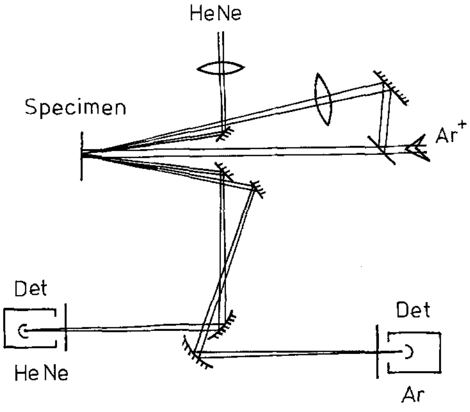

Fig. 1. Experimental two-probe layout for thickness measurement

A second probe beam from a HeNe laser is also focused in a similar manner in the same place. The intensites of these two probe beams are insufficient to cause measurable heating of the substrate. The reflected beams are monitored by separate detectors equipped with appropriate filters, and situated at the respective conjugate foci (with respect to the specimen) of two toroidal mirrors so that any deflection of the probe due to thermal expansion effects in the substrate or slight non-specularity of the reflected beam does not manifest itself by variations in the detector signal. Alignment of the whole is performed at the beginning of each experimental run by maximizing the probe signals from the very earliest stages of oxidation. Figure 2 shows the signals typically obtained from the two detectors during laser-induced oxidation.

The maxima and minima are due to interference effects in the growing oxide layer and may be compared to calculated spectra and thus used as a monitor of oxide film thickness at the centre of the irradiated zone.

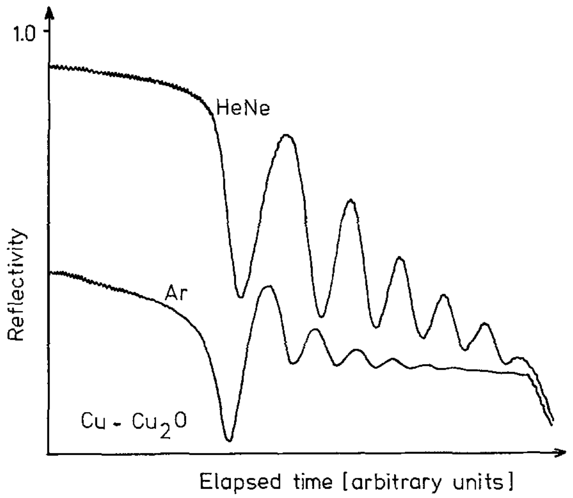

Fig. 2. Typical probe signals from the apparatus of Fig. 1

1.1. Specimen Preparation

The specimen substrates were, in most cases, 1 mm thick Pyrex 7740 slides, having room temperature $K = 9.15 \times 10^{-3}$ W/cm/°C, $\alpha = 5.1 \times 10^{-3}$ cm^2/s, values checked by us and in good agreement with manufacturers' data. After chemical and glow-discharge cleaning the substrate were coated with a film of either Cu or Cd evaporated at $\simeq 10^{-6}$ Torr from an appropriate source. Film thickness varied, but was generally in the range 1000–5000 Å monitored either with a quartz microbalance deposition or retrospectively using a Tolanski technique.

The quasi-normal spectral reflectivity of as-deposited films was measured at 633 nm and 481/514 nm. Cd films, with a coarse granular structure, displayed also a strong diffuse component of reflectivity which was measured as a function of scattering angle, again for quasi-normal incidence, at 481/514 nm. Diffuse scattering was negligible for Cu. The prepared specimens were mounted in the experimental arrangement of Fig. 1. Some experiments were conducted in a controlled atmosphere but since no marked effect of oxygen partial pressure was noted for oxygen pressures above a few tens of Torr, and the presence of a cover glass caused some experimental difficulties, most irradiations were performed in air.

2. Temperature Estimations

The estimation of film temperature in the central 50 µm dia or so of the laser spot during irradiation presents considerable problems; various methods which have been explored during the progress of this work are discussed below:

2.1. Measurement

A direct measurement of spot-centre film temperature can be attempted using a thermocouple constructed from 25 $\mu m^{\varnothing}$ wire. Even mechanical contact can be sufficiently good to give a faithful measurement of specimen surface temperature but the response time is slow due to the thermal inertia of the thermocouple wire, and direct heating of the latter by the laser beam also occurs. The obvious solution of irradiating from the rear side is not satisfactory since interference effects between the substrate faces give rise to fluctuations in the absorbed power. Also, since we are interested in possible laser enhancement of the oxidation process and comparison with previous work it is most desirable to irradiate the film surface exposed to the oxygen source, though we shall return to this point at a later stage.

Finally the front-mounted thermocouple poses obvious problems for probe measurements.

A better approach is a thin-film thermocouple deposited onto the substrate and covered with an insulating SiO layer prior to deposition of the metal film. Such thermocouples have been used by us but suffer from poor spatial resolution, difficulty in correct alignment, lengthy specimen preparation and, in our experience, poor reliability, particularly for the fine line width necessary in this application.

A third alternative is a fine thermocouple in contact with the back face of the substrate. If a number of specimens are prepared with differing thickness of support glass in 140 μm increments, and each irradiated by adjusting the laser power to produce equal effects in equal times than the measured rear face temperature may be extrapolated to zero thickness. We have found that such a procedure can predict temperatures in excellent agreement with the thin film technique above, but suffer also from the difficulties of poor spatial resolution, slow response and time-consuming preparation.

An indirect measure of substrate temperature can also be obtained by counting reflectivity minima during the heating or cooling cycle due to the interference effects between the substrate faces, when illuminated from the rear with a HeNe laser. For uniformly heated substrates temperature minima occur every 15°C or so, thermal expansion and temperature dependent refractive index accounting each for about half the observed effect. For front-surface heating a knowledge of the qualitative form of $T(0,z,t)$ permits an estimate of front surface temperature. This method, however, fails when the 451/514 reflectivity starts to fall since even the qualitative form of $T(0,z,t)$ is no longer easily obtainable.

2.2. Calculations

For the experimental conditions given the "thin film-long time" approximation is always valid, i.e. the role of the metal film is as a photon/thermal convector whose thermal capacity can be considered as negligible. We can also easily show that, for all the experimental conditions described, radiative and convective losses are negligible so that the thermal behaviour is controlled by diffusion in the substrate, whose front surface temperature is also the film temperature. For times $\lesssim 1$ s the substrate can also be treated as semi-infinite so that the expression for Gaussian heat flux at the surface of a semi-infinite solid applies [11].

The temperature rise at the spot centre is thus

$$T(0,0,t)=\frac{P_{\mathrm{incid}}(1-R)}{k\pi^{3/2}d}\tan^{-1}\sqrt{\frac{4\alpha t}{d^2}}, \qquad (1)$$

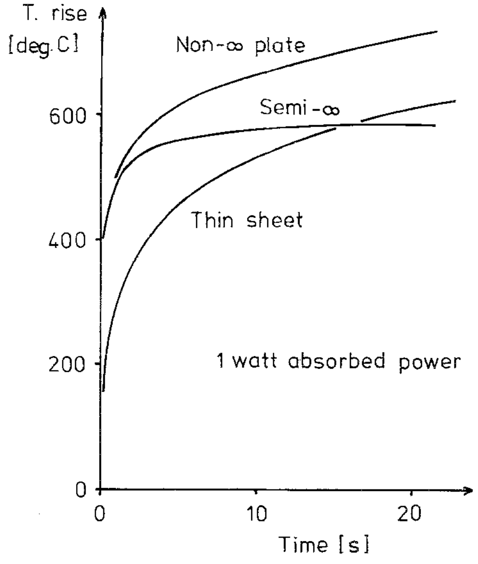

Fig. 3. Evolution of $T(0,0,t)$ for a Gaussian profile beam incident on glass substrate – various approximative geometries

where K and α are the thermal conductivity and thermal diffusivity of the substrate and d is the Gaussian radius at 1/e points.

For times $\gtrsim 1$ s we may also calculate numerically the axial temperature profile $T(0,z,t)$ for the semi-infinite solid and treating the substrate faces as thermal corrected front surface temperature of the substrate as a plate (Fig. 3). It is worth noting that the thin-plate approximation, also shown here, where temperature uniformity within the substrate thickness is assumed, is never a good approximation for the front-surface temperature. The thermal properties of the substrate are slowly varying functions of temperature in the range studied so that calculation, as described, can give a reasonable estimate of maximum film temperature up until the point where the reflectivity at 481/514 nm starts to fall due to oxide growth. From this point of view calculation of spot-centre temperature becomes exceedingly tricky.

Clearly the immediate effect of the fall in R will be an increase in spot-centre temperature, though by no means so great as would be predicted by changing R in (1) since the drop in R first occurs only at the spot centre. Indeed at some later time the central R returns to its initial value whilst there now exists a low-reflectivity ring around the centre. Evolution of the spatial profile due to absorbed energy is complex and demands a precise knowledge of the radial dependence of R with time. To further complicate matters this radial dependence is also a function of the time scale of the oxidation process, – lower powers with longer times produce larger oxidized spots.

Thus, whilst detailed knowledge of $R(r, P, t)$ would, in theory, permit a (lengthy) compution of $T(0, 0, t)$ both the measurement and the calculation are sufficiently difficult in practice as to deter us from this approach.

3. Results and Discussion

3.1. Cd *Films*

Although Cd films suffer, from an experimental point of view, from the disadvantage of appreciable diffuse reflectivity they offer one advantage best displayed by reference to Fig. 4, which shows the HeNe probe signal from the start of irradiation. The sharp drop in R at t_1 is due to melting of the Cd film. Interruption of the primary Ar^+ beam at t_2 causes a virtually synchronous increase in R, to a slightly higher than initial value (optical examination of the film at this point reveals a faint shiny patch). The Ar^+ beam is reapplied at t_3 and the later fall in R at t_4 corresponds to remelting, fitting exactly with a temperature calculation carried out as described for a finite plate and using Duhamel's theorum. We have thus a useful calibration point built into the experimental curves. Using this, and calculating in the same way we find the temperature at the onset of oxidation to CdO to be ± 400°C, depending on the laser power, and hence on the time scale involved.

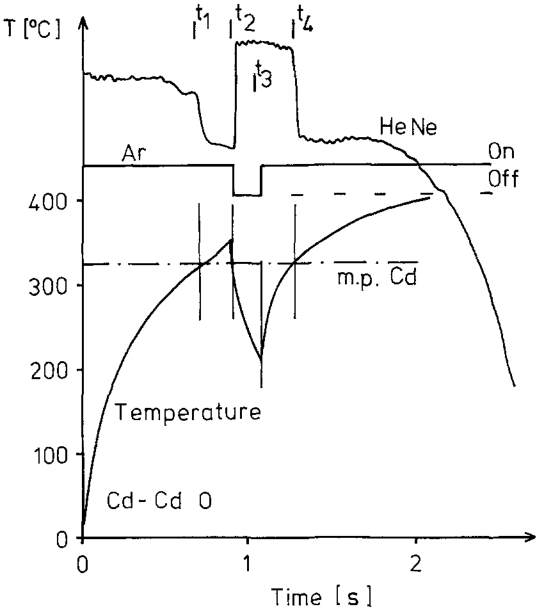

Fig. 4. Beam chopping just after melting of a Cd film and its use for temperature calibration

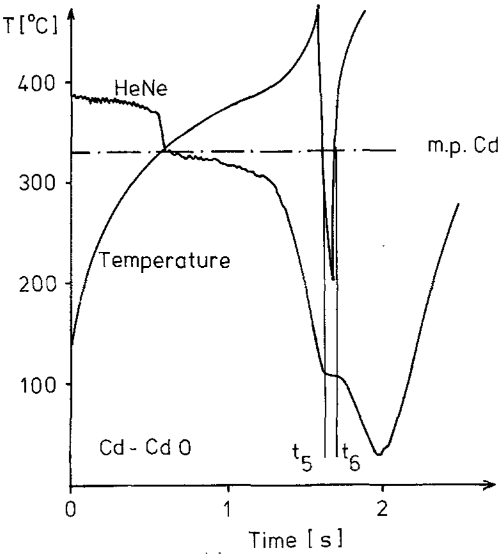

Fig. 5. Beam chopping during oxidation of a Cd film with temperature modelling

Figure 5 shows the effect of momentarily interrupting the Ar^+ beam at a later stage of oxidation. Growth of the oxide layer, as indicated by the HeNe probe, ceases abruptly at t_5, and recommences almost equally abruptly, albeit at a lower rate, at t_6.

We have previously [6] interpreted this behaviour as due to a non-thermal contribution to the oxidation process, since finite plate calculations do not predict temperature fluctuations rapid enough to explain the observed effect. However, a two probe experiment shows that well before t_5 the Ar^+ central point reflectivity has fallen to about a quarter of its initial value. The effect of this low reflectivity zone at the beam centre is to locally increase the temperature and, more importantly, to introduce a steep temperature gradient into the near surface region of the surface region of the substrate since the effective diameter of the hot spot is small. It results that the rate of temperature charge at t_5 and t_6 is greater than previously calculated and is sufficient to traverse the melting point of Cd in times comparable to the time resolution in Fig. 5. (See temperature modelling in Fig. 5.) Since the melting point of Cd might be expected to represent a discontinuity in the oxidation rate, the experiment thus described does not then, in fact, preclude a purely thermal explanation of the observed behaviour. We note also that there is no advantage to be gained from the greater time resolution obtained by working at higher laser power and concomitantly reduced time scale, since the temperature gradients induced in the substrate, and hence the rates of surface temperature fluctuations are likewise so much the greater.

We conclude that the laser induced oxidation of Cd remains at least compatible with a purely thermal model although the existence of a phase change, the high diffuse component of reflectivity, and the paucity of comparable published data do not make Cd the ideal material for further study in the elucidation of basic mechanisms.

3.2. Cu *Films*

The exposure of Cu films to the primary Ar$^+$ beam at incident power exceeding ± 1 W results in the formation of Cu_2O. For thick films and/or high laser powers further oxidation to CuO occurs, apparently upon completion of the Cu_2O layer, and in the form of irregular shaped islands on the film surface, often associated with buckling and partial detachment of the oxide layers from the substrate. Such formation is poorly suited to a probe experiment and here we limit the discussion to the early stages of Cu_2O formation.

The HeNe and Ar$^+$ probe signals from a 2500 Å thick film are shown in Fig. 6. The form of these curves remains essentially the same for incident laser powers between 1 and 14 W and in Table 1 we summarise, for this power range, the calculated oxidation rate at the start of the first decrease in HeNe reflectivity and the calculated temperature, ignoring for the moment the effects of reflectivity charges at 481/514 nm.

These temperatures can thus be expected to be systematically low though probably not by too much since we are dealing with the early stages of oxidation (Point A on Fig. 6), i.e. before the drop in Ar$^+$ reflectivity has had time to establish a large effect. Note that, particularly at high laser power, the temperatures are well above the softening point of the glass substrate but that this temperature is maintained only for a short time $\simeq 20$ ms at 14 W and is limited to a very shallow surface, region of the substrate. Thus the substrate does not deform, though it sometimes cracks.

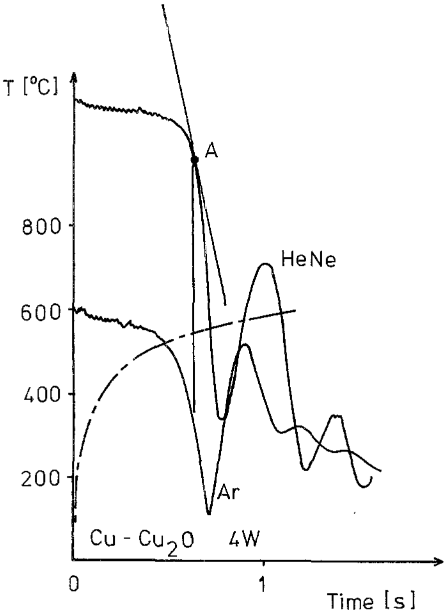

Fig. 6. Two probe signals during oxidation of Cu films. Determination of the oxidation rate at *A*

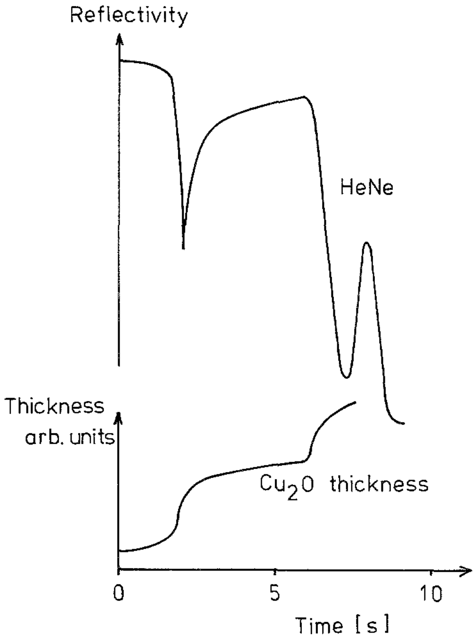

Fig. 7. Oxidation of a Cu film with an efficient heat sink, showing the feedback effect

Note also that the overall temperature fluctuations introduced by the complex changes in $R(r, t, P)$ at 481/514 nm and subsequent thermal diffusion in the substrate cannot be too dominant since the general shape of the NeNe probe signal in Fig. 6 indicate a smooth progression of the central oxidation reaction, apparently following an approximately linear growth law and exhibiting only slight asymmetry of the peaks due to these effects. This point is dramatically illustrated by Fig. 7. Here the Cu film is deposited on a 140 µm thick glass substrate mounted in intimate thermal contact with a massive Cu block serving as a heat sink.

In this geometry the essentially one-dimensional nature of the heat diffusion equation and the small dimension, which allows equilibrium to be reached rapidly, mean that changes in surface reflectivity are quickly and effectively translated into fluctuations in surface temperature.

This results in large cyclic variations in the film temperature, which are reproduced in the oxide growth rate. This configuration is perhaps poorly suited to kinetic studies but it already provides an important indication of the essentially thermal nature of the oxidation process. It was pointed out in the introduction that one of the problems associated with the study of laser induced reactions is that few other heating techniques allow a comparable rate of energy coupling into the film, particularly whilst at the same

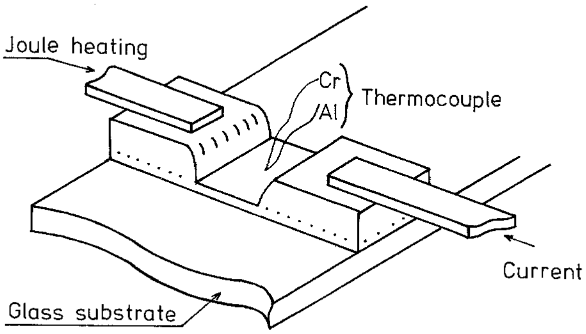

Fig. 8. Specimen for oxidation of Cu by Joule heating

time permitting access to an oxygen atmosphere, so that comparative data can be difficult to obtain.

To approach this problem a series of specimens were prepared as in Fig. 8. The 2500 Å thick Cu film was deposited via a mask to form 5 mm wide strips and ±2 µm thick Cu pads deposited on either side of a 3 mm × 5 mm central zone. An electrical current is passed through this zone via mechanical contacts to these pads. Voltage and current were independently monitored and a system devised for holding the dissipated power constant, at least until complete oxidation of the central zone abruptly increases the overall resistance by several orders of magnitude.

The HeNe probe signal from the center of the zone is shown in Fig. 9, together with the temperature signal derived from a 25 µm$^{\varnothing}$ Cr/Al thermocouple in mechanical contact with the film. The measured temperature is in reasonable agreement with that calculated by assuming constant power dissipation over the area of the sample although such calculation is inexact after the start of oxidation since this occurs preferentially at the zone center and hence presents a non-uniform resistivity of the sample. Figure 9 and Table 2 shows that oxidation occurs following an approximately linear growth law at rates temperatures entirely compatible with Ar$^+$-laser-induced oxidation, and thus, clearly, with a thermal model for the latter.

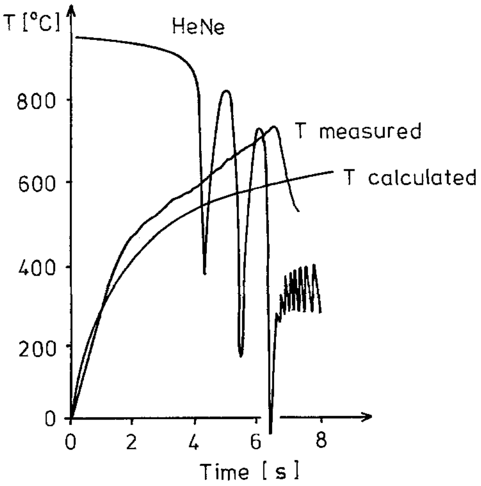

Fig. 9. Oxidation of Cu film by Joule heating with measured and calculated temperatures

This view is further supported by the rather simple experiment of irradiating the sample from the rear side. Although the above-mentioned interference effects in the substrate here result in non-uniform heating, it is nevertheless clear that, after taking due account of the losses due to reflection by and absorption in the substrate, oxidation proceeds at a comparable rate in this configuration and therefore, since virtually no light reaches the active oxide layer, must be primarily due to heating of the thin film.

There remains only the question of whether an essentially thermal effect might be enhanced by the absorption of laser light, or indeed any high intensity light, since the precision of the temperature measurements and calculations do not allow us to exclude such a possibility.

To look for possible effects we heated a 1 mm thick Cu sheet from the rear side using a hot air paint stripper to ±500°C, whilst at the same time exposing the front side to the unfocussed Ar$^+$ beam of 10 W incident power, sufficient to give additional calculated temperature rise of ±8°C.

The hot-air blower was positioned asymmetrically so that after 5–10 s broad interference bands were produced in a wedge shaped Cu_2O layer on the copper sheet.

Close visual inspection of the specimen after this treatment revealed no trace whatsoever of the point of laser impact.

We turn finally to a closer examination of the data derived for Cu oxidation by either method, since the experiments strongly support the view that they result from the same oxidation mechanism and are therefore compatible. Using the data in Tables 1 and 2, Fig. 10 shows an Arrhenius plot of Cu_2O growth rate from which we derive an activation energy of ±0.65 eV. We

Table 1. Ar$^+$-laser-induced Cu oxidation

Laser power [W]	Calculated temperature [°C]	Cu_2O growth rate [µm/s]
3	495	0.093
4	540	0.197
5	660	0.26
6	695	0.55
7	785	0.89
8	825	1.29
9	840	1.60
10	865	1.49
12	890	1.92

Table 2. Joule-heating-induced Cu oxidation

Dissipated power [W]	Calculated temperature [°C]	Cu_2O growth rate [μm/s]
3.5	495	0.049
4.5	525	0.10
5.0	555	0.13

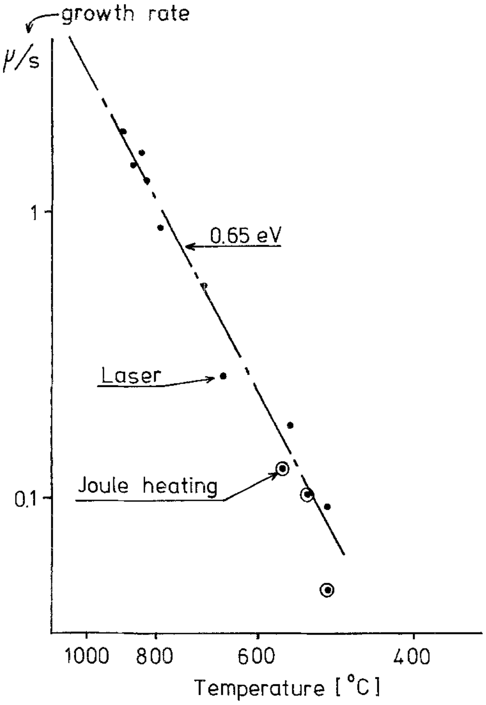

Fig. 10. Arrhenius plot of oxidation rate of Cu films vs. temperature

have already noted that the growth law appears to be linear.

In Fig. 9 we see that the interval between the second and third reflectivity minima is, in fact, slightly less than that between the first and second, which would imply an acceleration of growth rate at constant temperature. Using, however, the predicted temperature increase in this interval and the value of activation energy derived above we find that a linear growth law does precisely fit the data represented by Fig. 9.

4. Discussion

The experiments described show that cw Ar$^+$-laser-induced oxidation of Cu films, under our experimental conditions, is due to the heating effect of the laser beam. No other effect is observed. Classical studies of Cu oxidation in oxygen atmosphere show that at

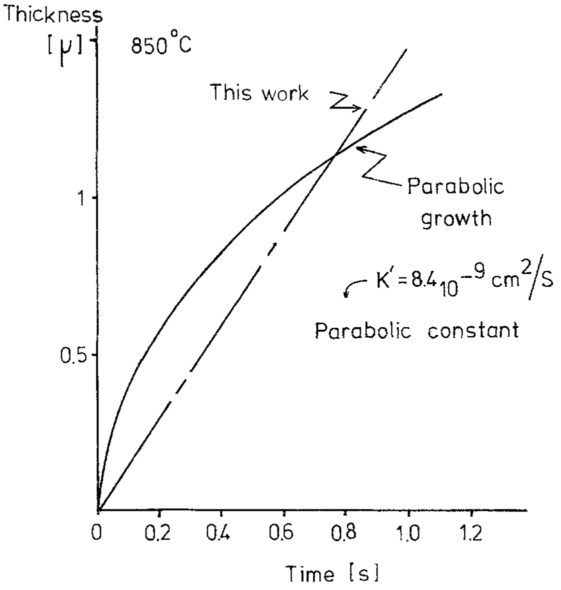

Fig. 11. Comparison of the present work with diffusion limited oxide growth according to the Wagner theory

temperatures and O_2 pressures in the range studied here, oxidation normally proceeds according to a parabolic growth law with the rate limiting step being the diffusion of Cu ions and electrons in the Cu_2O layer [12].

The activation energy for diffusion is given as ± 1.65 eV and the rate constant at 850°C for, e.g., is $\pm 8.4 \times 10^{-9}$ cm^2/s. For a 400 Å thick oxide layer, i.e. about the thickness to which the data of Table 1 refers, the growth rate should thus be $\simeq 20$ μm/s. The fact that we observe experimentally a rather lower growth rate and linear growth law indicates that at this combination of thickness and temperatures the rate limiting step is a phase boundary reaction – probably that at the Cu_2O/O_2 phase boundary [12] occuring with an activation energy of 0.65 eV derived in Fig. 10 (see Fig. 11, too).

It is worth noting that this regime of oxide growth is practically inaccessible other than by techniques such as described, since it is only maintained for at most a few seconds at these temperatures.

There have appeared several reports [1–3] in the literature of cw CO_2-laser-induced oxidation of Cu where the authors claim a non-thermal effect. The explanations of the discrepancy between these works and the present one may be due to the fact that in the former the conditions are such as to place one squarely in the diffusion limited regime, although calculations suggest that at the lower end of the temperature range studied here diffusion should also be rate limiting, and the final experiment described is carried out under these conditions. It would be curious if a photonic, rather than thermal effect, was present at 10.6 μm and not at 481/514 nm.

5. Conclusion

Ar^+-laser-induced oxidation of thin Cu films in air is a thermal process resulting from the heating effect due to the laser beam. This conclusion is not necessarily incompatible with other studies reported where a non-thermal model appeared appropriate since the growth regimes are different. Laser-oxidation studies are complicated by the feedback phenomenon of surface reflectivity which means that temperature estimations are difficult except in the very earliest stages of oxidation. Thus, whilst laser irradiation may give access to previously largely unexplored growth regimes these might also be accessible by alternative techniques, e.g., joule heating, without the inherent problems of feedback.

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