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Kinetics and mechanism of oxide formation on Cr thin films

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Abstract. Oxidation kinetics of thin films of Cr in the temperature range 490–630 °C have been studied using backscattering spectrometry and x-ray diffraction. In the studied region the growth of the oxide Cr_2O_3 has been found to obey a parabolic growth-rate law with an activation energy of 1.2 eV. Implanted Xe markers show that the growth of the oxide occurs almost entirely at the surface and is controlled by the motion of Cr species in the oxide.

1. Introduction

Many studies have been performed of the oxidation mechanism and measurements of the kinetics for oxidation of Cr [1–17]. Most of the data are on oxidation of bulk specimens and oxidation at temperatures above 900 °C. The present investigations deal with oxidation of Cr thin films at lower temperatures There have also been some investigations in the literature covering essentially the present range of parameters. We will, in the following, sketch the general trends observed for Cr oxidation.

Cr_2O_3 is the oxide that most frequently grows on Cr. The measurements of growth rate constants show a large spread, apparently caused by a strong dependence on surface preparation techniques and crystal orientations. It is generally found that at high temperatures the growth is dominated by Cr motion, and a rather high activation energy, typically around 2.6 eV. In single crystals it always seems to be the case that Cr is the fastest moving species. In polycrystalline oxides diffusion of oxygen species has been inferred from the compressive stresses of the oxides, where growth within the oxide has been suggested, and cracks have been observed. Intuitively one could think that the diffusion mechanism associated with oxygen diffusion would then have a lower activation energy. At temperatures below 900 °C (600–900 °C) it is generally observed that the activation energy for oxide growth becomes lower, namely around 1.6 eV. It is not obvious that Cr would be the most mobile species for growth at low temperatures. Hope and Ritchie [10] have performed oxidations on specimens with porous Pt electrode markers. These measurements indicated that Cr is the fastest moving species. We feel that an independent measurement by another marker technique can be justified, since by most techniques the result could hypothetically depend on the procedures used.

In § 2 we describe how the samples of the present investigation were prepared together with other experimental details. In § 3 we present data on the oxidation growth rate. We also present the results of marker experiments to find the relative mobilities of

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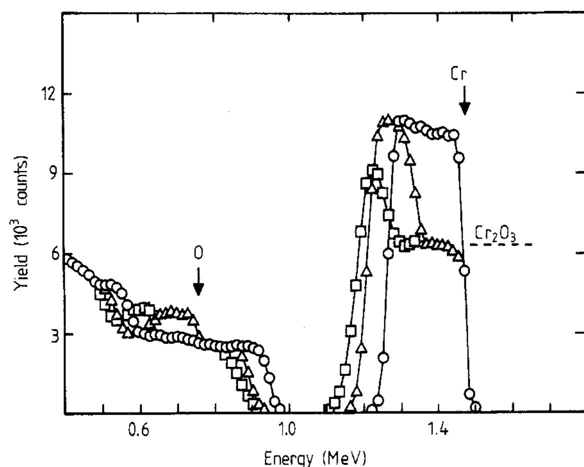

Figure 1. 2 MeV $^4He^+$ backscattering spectra of a Cr film on an oxidised silicon wafer; as deposited (○), and after oxidation at 630 °C for 20 min (△) and 105 min (□). The energy for scattering from Cr and oxygen are marked. The growing oxide is Cr_2O_3.

metal and oxygen species during oxide growth. In § 4 we will discuss the results in light of previous studies on the oxidation of chromium and diffusion in chromium oxides.

2. Experimental

Oxidised single crystal silicon wafers were used as substrates for electron-gun evaporated thin films of Cr. Typical thicknesses of the films were 110 nm and typical evaporation rates were 0.5 nm s^{-1}. The wafers were cut into individual pieces and the metal films were oxidised in dry oxygen at a flow rate of 1 l min^{-1} at atmospheric pressure over various times and temperatures.

For Kirkendall marker experiments [18, 19] we used sets of samples which were first oxidised for a short time to yield an oxide typically of thickness 50 nm. These samples were then ion-implanted with 80 keV Xe ions at a fluence of 1×10^{15} ions cm^{-2} to yield a distribution of Xe within the oxide. The samples were then oxidised further with the Xe acting as a Kirkendall marker. The motion of the marker relative to the surface then gives information on the relative mobilities of metal and oxygen during oxide growth.

For analysis of the depth distribution of metal and oxygen we used standard 2 MeV $^4He^+$ backscattering spectrometry. X-ray diffraction with Cu Kα radiation was used to identify oxide phases. For parametrisation of the kinetic data we use the relationship $\Delta x^2 = B(t + t_0)$ where Δx is the oxide thickness and t is the oxidation time. The constant B will henceforth be called the parabolic rate constant. t_0 is a fitting parameter to account for the initial non-parabolic growth. To convert energy loss in backscattering spectra to oxide thickness we used Bragg's additivity rule with standard semi-empirical stopping cross sections [20] which yield the number of atoms per unit area. In order to get the corresponding thickness we have assumed a bulk density of 1.04×10^{23} atoms cm^{-3} for Cr_2O_3.

3. Results

3.1. Cr oxidation kinetics

Figure 1 shows backscattering spectra obtained for the oxidation of Cr films at 630 °C for varying times. The growing oxide gives rise to the plateau in the Cr signal of the

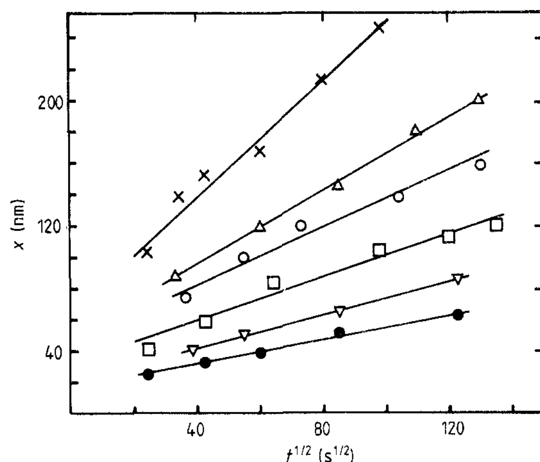

Figure 2. Oxide thickness plotted versus square root of oxidation time for Cr films oxidised at 490 °C (●), 520 °C (▽), 550 °C (□), 575 °C (○), 600 °C (△) and 630 °C (×).

spectra. This oxide has been identified by x-ray diffraction to be Cr_2O_3 in agreement with the backscattering results. The time dependence of the thickness of the oxide is shown in figure 2 for oxidation at various temperatures. The growth nearly obeys a parabolic law, but it is seen that the straight lines fitted to the data do not go through the origin. This is probably due to an initial fast-oxidation regime as reported previously [6, 7]. However we have not investigated this regime in any detail. When the growth rate measurements are plotted in an Arrhenius plot as shown in figure 3, the best fit to the data is with a growth rate constant

$$B = 1.1 \times 10^{-7(\pm 1)} \exp[(-1.2 \pm 0.1)\,\mathrm{eV}/kT]\,\mathrm{cm}^2\,\mathrm{s}^{-1}.$$

It can be seen that the data point at 630 °C ($1/T = 1.1 \times 10^{-3}\,\mathrm{K}^{-1}$) is relatively far off this line. One can speculate as to whether this signals the onset of another diffusion mechanism at higher temperatures.

3.2. Cr marker experiments

Figure 4 shows a backscattering spectrum of a Xe-implanted partially oxidised Cr film together with the spectrum of an identical sample oxidised further after the implantation. It is seen that the centroid of the Xe marker has moved towards lower energies, meaning that the marker is located deeper into the sample for the more highly oxidised film. (The change in energy position of the marker is about twice that of the lower energy edge of the Cr signal and about the same as the increase of the width of the plateau corresponding to the Cr_2O_3 oxide.) This is what one would observe when the growth of the oxide occurs at the surface by migration of Cr atoms through the oxide, if we assume that the Xe distribution acts as a Kirkendall marker.

4. Discussion

We observe a parabolic growth of Cr_2O_3 upon oxidation of Cr thin films. We will first compare the value of the activation energy we have observed with those observed in the literature. It is natural to compare the present data with those of Alessandrini and Brusic [6]. They have observed an initial rapid linear growth followed by a parabolic one. Their

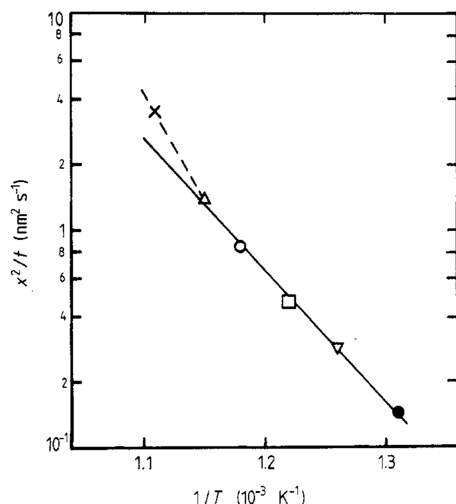

Figure 3. Arrhenius plot of the growth rate determined from figure 2, for Cr_2O_3 oxide growth (symbols as defined in figure 2).

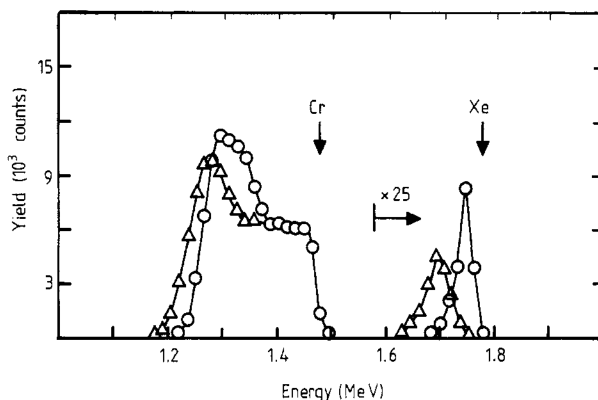

Figure 4. 2 MeV $^4H^+$ backscattering spectra of a Cr film oxidised at 550 °C for 80 min and then implanted with Xe (○) and the spectrum after this sample is oxidised for a further 160 min at 550 °C (△). The sample is tilted at 45° with respect to the beam direction. The figure shows the scattering yield from Cr and Xe.

measurements for the activation energy of the parabolic growth rate constant was 1.00 ± 0.02 eV. Our value of 1.2 ± 0.1 eV is slightly larger than this. The conditions for the oxidation seem rather similar in the two cases, whereas Young and Cohen [7] report an activation energy of 1.6 eV for oxidation at a partial oxygen pressure of 0.5 Pa. It should be appreciated that in all cases the activation energy for growth of Cr oxide on thin films in the temperature range 400–600 °C is appreciably smaller than that observed for Cr oxide growth (on bulk samples) at higher temperatures.

As shown in figure 2 the extrapolation to zero time of the straight-line-fits to our data neither passes through the origin, which would occur if the oxide grew by a parabolic rate constant from zero oxide thickness, nor through a common point for all temperatures, which would occur if a significant oxide scale had grown prior to the oxidation at the elevated temperature. Thus the data indicates an initial fast oxidation at the oxidation temperature. Young and Cohen have studied the fast initial oxidation in more

detail [7]. They get best fit to their data with a Mott–Cabrera type rate equation, whereas Alessandrini and Brusic [6] suggest a fast initial linear rate, apparently without considering other kinetic laws. Both studies of the initial fast oxidation has been carried out on thin films in the temperature range 300–600 °C. Whether these two oxidation studies actually reveal different initial mechanisms or not is not the purpose of the present discussion. The point is that our data can be explained by an initial fast oxidation, which we have not studied in any detail, and phenomenologically an initial fast diffusion seems to be the rule rather than the exception.

The parametrisation of the kinetic data should be discussed in light of the results from the marker experiment. We have found that the chromium oxide grows by Cr atoms migrating to the surface where they are oxidised, essentially in agreement with the porous Pt marker electrode measurement of Hope and Ritchie [10]. When that is the case one can in principle deduce parameters which are directly linked to the physical oxidation mechanism. It is reasonable to assign the activation energy of the oxide growth as an effective activation energy associated with the transport of Cr species in the oxide. In general it is possible to observe a parabolic growth of an oxide either if the growth is controlled by diffusion under local equilibrium conditions or alternatively if it is controlled by migration of ions in an electric field under local non-equilibrium conditions. One should deduce from these models the appropriate parameters. A comparison between their magnitude and a physically reasonable magnitude could in favourable cases distinguish between possible diffusion mechanisms.

We consider first the case that the growth of the oxide may be controlled by the diffusion of Cr species under local equilibrium conditions. The diffusivity has often been estimated from the parabolic rate constant by the Nernst–Einstein relationship [21]. We reproduce the necessary assumptions in the following. The flux j of Cr atoms is given by Fick's first law

$$j = -D(\mathrm{d}C/\mathrm{d}x) \tag{1}$$

where D is the diffusivity of Cr atoms in Cr_2O_3, C is the concentration and x is the oxide thickness. The instantaneous growth rate is given by

$$\mathrm{d}x/\mathrm{d}t = j/\nu N \tag{2}$$

where N is the atomic density of Cr_2O_3 and ν is the fraction of Cr atoms in the oxide. One now considers the gradient in the chemical potential μ of Cr atoms as the driving force for the diffusion of Cr atoms. The difference across the oxide is the Gibbs free energy of formation of Cr_2O_3. Since the entropy difference is small, as is generally true for many solid-state reactions, one approximates the chemical potential difference with the heat of formation, ΔH, per Cr atom [22, 23]

$$\mathrm{d}\mu/\mathrm{d}x \simeq \Delta H/x. \tag{3}$$

The chemical potential is given by

$$\mu = kT \ln a \tag{4}$$

where a, the activity of Cr, is given by

$$a = \nu\gamma \tag{5}$$

here γ is called the activity coefficient. If for the purpose of easy calculation one now assumes constant molar volume in the Cr_2O_3 phase one has

$$C = \nu N. \tag{6}$$

Alternatively this relation can be used to define ν. By combining equations (1)–(6), one

obtains a differential equation with a solution which can be brought to the form $x^2 = B(t + t_0)$. It is easily shown that the relationship between the parabolic rate constant B and the average diffusivity is then

$$\bar{D} = (BkT/2\Delta H)[1 + \mathrm{d}(\ln \gamma)/\mathrm{d}(\ln \nu)]. \tag{7}$$

Here the differentials should formally also be regarded as averages. For ideal or dilute solutions γ is constant, so the last term in the parentheses vanishes. Even if this is not generally true this term has often been neglected [24–26]. One then obtains

$$\bar{D} = BkT/2\Delta H. \tag{8}$$

This diffusivity should then formally be termed the 'Nernst–Einstein diffusivity'. When the average diffusion coefficient of Cr in Cr_2O_3 is written in the usual form as

$$\bar{D} = D_0 \exp(-Q_D/kT) \tag{9}$$

and one defines a function $F(T)$ as

$$F(T) = \ln B - \ln(2\Delta H/kT) \tag{10}$$

we see that we have

$$F(T) = \ln D_0 - Q_D/kT \tag{11}$$

so that a plot of $F(T)$ versus $1/T$ will yield D_0 and Q_D by a linear fit. Of course, the activation energy for the average diffusivity will be close to that of the parabolic growth rate constant, namely 1.2 eV. The pre-exponential diffusion constant D_0 becomes around 1×10^{-9} cm^2 s^{-1}. One realises that this value in any case will be a very crude estimate considering the uncertainties involved, where errors in the activation energy will have a large effect, and also considering the approximations used. It has been stated that the pre-exponential diffusion constant for vacancy diffusion in metals should be around 1 cm^2 s^{-1} [24]. The magnitude of the pre-exponential diffusion constant estimated from our experiments is smaller than this. When D_0 is derived from statistical mechanics it is often written in the form [13]

$$D_0 = \alpha\kappa\omega_0 a^2 \exp(\Delta S/k) \tag{12}$$

where α is essentially a geometrical factor, ω_0 is approximated by the Debye frequency, κ is the 'transmission coefficient' which is the probability that an atom with sufficient energy to make a jump actually will complete it (for self-diffusion in elemental metals $\kappa = 1$), a is the jump distance and ΔS is the change in entropy. For vacancy diffusion the latter is the sum of the vibrational entropy of the vacancy and the entropy of migration. For interstitial diffusion ΔS is the entropy of migration. Equation (12) puts a lower limit on the value D_0 if the diffusion can be described by its implicit assumptions. Since $\Delta S = -\mathrm{d}(\Delta G)/\mathrm{d}T$ and it is improbable that ΔG will increase with temperature, it is probable that ΔS is positive. A negative ΔS is not theoretically impossible but is regarded as highly improbable [27]. A lower limit for the value of D_0 from (12) will be around 4×10^{-3} cm^2 s^{-1} and will most probably be higher for vacancy diffusion. In this context one would like to think that smaller values could be evidence for short-circuit diffusion. In the present case this might be tempting, also considering the low activation energy found in our experiment.

We now turn to the possibility of migration of Cr ions in an electric field. The parabolic rate constant B under such conditions has been deduced to be $B = 2\Omega a\omega_0\varphi sq/kT$ [28, 7], where s is the surface concentration of the injected species responsible for mass

transport, φ is the electrostatic potential difference, q is the charge of moving species, ω_0 is the lattice vibration frequency, a is the jump distance, and Ω is the volume per Cr atom. By inserting $\Omega = 2.4 \times 10^{-23}\,\mathrm{cm}^3$ and $a = 0.2\,\mathrm{nm}$ we get a value of 10^{10}–$10^{11}\,\mathrm{V\,cm}^{-2}$ for the term φs in the temperature range measured. It has been stated that this is a reasonable value [7], meaning that the diffusion mechanism could possibly be described by this mechanism.

When describing diffusion in oxides in particular, one is interested in the charge state of native defects and of migrating species. We note that at high temperatures Cr_2O_3 is a p-type conductor and the important defect reaction taking place is considered to consist of Cr substitutional atoms dissociating into triple negatively charged vacancies, a doubly charged Cr interstitial and a hole [13]. In general a transition from intrinsic to extrinsic diffusion may take place when the temperature is lowered from high temperatures, where the native point predominate, to low temperatures, where the point defect concentrations are determined by the impurity concentration. In such a case D_0 can be written as

$$D_0 = N_\mathrm{d} \alpha \kappa \omega_0 a^2 \exp(\Delta S/k) \tag{13}$$

where N_d is the fraction of lattice sites occupied by point defects that take part in the diffusion, ΔS is the entropy of migration and the other symbols have essentially the same meaning as in (12). It is clear that if N_d becomes temperature independent then the value of D_0 can become lower than the lower limit given by (12).

We therefore conclude that even if the present analysis alone cannot give the growth mechanism, it appears that a lattice diffusion under equilibrium conditions does not seem reasonable. It is tempting to invoke a fast diffusion mechanism along grain boundaries or dislocations to explain the measured diffusivity. The activation energy of the growth process appears considerably smaller than the activation energy for Cr tracer diffusion measured at high temperatures [1]. The latter is around 2.65 eV. One would obviously have to invoke different controlling mechanisms at high and low temperatures.

5. Summary

We have observed oxidation of Cr thin films in the temperature range 490–630 °C and found the growing oxide to be Cr_2O_3. By implanted Xe marker studies we have found that the growth occurs at the surface by Cr species migrating through the oxide. The growth rate law is parabolic after a short rapid oxidation. Measurements of the parabolic rate constant yields

$$B = 1 \times 10^{-7} \exp[(1.2 \pm 0.1)\,\mathrm{eV}/kT]\,\mathrm{cm}^2\,\mathrm{s}^{-1}.$$

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