Fig. 2 The time changes in ellipsometric parameters and the current are indicated for 4100 Å. Initial passive values for 20 h film growth are shown at the far left. Chloride was introduced from 0 to 43 min. The cross-hatched area indicates the period during which solution was changed back to non-chloride solution. At 120 min the passive values had been recovered and the entire experiment was then repeated.

monitored to determine whether any changes in the film took place on removal of the chloride. The time period above 50 min in the graph of Fig. 2 shows that the original passive, steady-state values of Δ and ψ were again attained in about 80 min. The passive film, as characterized by its ellipsometric parameters, had been recovered. The steady-state values are shown again at 120 min.

It can now be asked whether this recovered passive film, as characterized by its resistance to breakdown by chloride, is also comparable to the original passive film. To find the answer, the chloride environment was reintroduced at 122 min in Fig. 2 to the recovered passive film, and the entire process repeated. The symmetry of the curves on the left and right in Fig. 2 leaves no doubt that the recovered film has all of the usual properties attributed to the passive film.

These observations then indicate that, prior to breakdown, the chloride is involved in an alteration of the film, for example, a slow penetration of the chloride into the film to fill defect sites or available lattice positions. Similar studies must first be made at the other wavelengths where this process can be observed (4700.0 Å and 4900.0 Å) before an actual mechanism is proposed. It is perhaps interesting to note that the three wavelengths at which optical changes were observed due to the chloride addition are close to wavelengths at which the Cl II (Cl^+) spectrum shows absorption peaks; 4132.48 Å, 4794.54–4896.77 Å (unpublished work of C. C. Kiess and T. L. deBruin). These exact wavelengths will be studied in future work on this system.

These studies show that the introduction of chloride ion produces subtle changes in the passive films on iron before the completion of catastrophic breakdown. It is also clear that the breakdown process can be successfully interrupted and reversed by introduction of a nonchloride environment, with full recovery of the passive film.

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Possible Evidence for Double Plasmons in Electron Energy Loss Spectra

RECENTLY, Crick and Misell¹ presented energy loss spectra of fast electrons which have passed through thin film specimens of germanium. The reported spectra had been analysed so as to remove plural scattering contributions and show a large peak at 15.6 eV, representing the single scattering single plasmon excitation process, and a small broad peak with a maximum near 33 eV. Crick and Misell interpret this peak as being due to the $M_{4,5}$ X-ray absorption edge of germanium at 32 eV, and point out that this is usually obscured by the multiple-loss peak due to the double scattering single plasmon excitation process.

I wish to suggest tentatively that the broad peak at 33 eV could be a composite one, consisting of the single particle X-ray transitions and also containing a contribution from the single scattering double plasmon excitation process. This second order process has been analysed theoretically by Ashley and Ritchie², who show that it can be a significant contribution to the loss spectrum peak at $2\hbar\omega_p$ (ω_p is the plasma frequency), which is usually dominated by the double scattering single plasmon excitation process.

The small peak in the spectrum of the 880 Å thick specimen reported by Crick and Misell can be decomposed into two peaks—a narrow double plasmon peak at 31.5 eV and a broader peak due to the single particle transitions above 32 eV. A comparison of the areas of the single plasmon peak and the double plasmon peak then gives a measure of the relative probabilities or mean free paths of the two processes. The resulting estimate is found to be

$$\frac{P_{2,1}(t)}{P_{1,1}(t)} = \frac{\lambda_p}{\lambda_{2p}} \approx 0.03$$

where $P_{1,1}(t)$ and λ_p are the probability and mean free path for the single plasmon process, and $P_{2,1}(t)$ and λ_{2p} are the corresponding factors for the double plasmon process. Following Ashley and Ritchie

$$\frac{\lambda_p}{\lambda_{2p}} \approx 0.0103 \quad r_s^2 \approx 0.041$$

using $r_s \approx 2$, the calculated interelectron separation for germanium. This reasonable agreement, however, must be considered in the light of (i) the necessarily large uncertainty involved in estimating the area of the double plasmon peak, and (ii) the theoretical value of λ_p/λ_{2p} is very sensitive to the cutoff wave vector k_c (being proportional to k_c^5) and an accurate value of this parameter is not known.

Additional evidence for the existence of the double plasmon (in aluminium) has been obtained using an entirely different method. The technique involves an extension of that described by Spence and Spargo³, in which the thickness dependence of the single and multiple-loss plasmon peak intensities have been measured and analysed in detail. The results of these experiments will be reported elsewhere.

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