

Note

Plasma Loss Spectra of Fe(100) Surfaces by Means of Low Energy Electron Reflection

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When a fast charged particle, for example electron, impinges on the metal, it will have sufficient energy to excite a plasma oscillation, and we may expect that these excitations will play a role in determining a manner in which the particle transfers energy to the metal. The plasma oscillation frequency or, in other words, plasmon excitation energy is one of the most important collective properties in the electronic structure of metals. The frequency of the bulk plasma oscillation is given by ¹⁾

$$\omega_p = (4\pi n e^2 / m)^{1/2}$$

where n , e and m are number density, charge and mass of electron. If the crystal surface is bounded by the layer which has the dielectric constant ϵ , the surface plasma oscillation has the frequency ¹⁾

$$\omega_s = \omega_p / \sqrt{1 + \epsilon}$$

A considerable number of experiments on the characteristic energy losses of KeV electrons in metals were carried out, in which the energy loss spectrum was analyzed with the aid of electrostatic focusing techniques. Prior to 1960, the majority of samples used were metallic thin films deposited and maintained in conventional high vacuum and the high energy electron transmission techniques were mostly employed. In spite of the poorly defined conditions on the sample purity, structure, thickness and surface cleanliness (carbon and oxygen contamination), the agreement between experimental values and theoretical expectations on bulk plasmons was thought to be very good in most non-transition metal groups.

In the case of transition metal groups containing Mn, Fe, Co Ni, Pt, Cu, Ag and Au, the agreement between observed values and theoretical expectations based on the free electron model was clearly bad even in the case of bulk plasmons. In general, there is a considerable scatter in energy loss values between different experiments carried out on the same metal. It is presumably attributed to considerable variations in the sample purity, initial contaminations and damage of the metal films produced by the deposits of impurities as a result of electron bombardment in dirty conventional high-vacuum conditions usually employed in such investigations. To obtain the accurate values of bulk and surface plasmons in metals, the atomically clean surface of high-purity bulky single crystal samples should be investigated by means of low energy electron reflection method. Recently, as a result of a rapid development of ultrahigh vacuum science and various

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electron spectroscopies to define solid surface conditions in atomic level, far more accurate investigations can be achieved on the determination of bulk and surface plasmon energy values of metals.^{2,3)} Concerning to the characteristic energy loss spectra of Fe thin films, several experimental results were already reported.^{4,5,6)} However, these works were performed with using non-defined polycrystalline Fe samples covered by heavy contaminations, and none of the results on the plasma loss spectra of Fe single crystal clean surface have been published until recently. It is the purpose of this paper to show the bulk and surface plasmon energy values of Fe (100) clean surface and their variation as a function of sulfur coverage on the surface determined by the low energy electron reflection method combined with LEED and Auger electron spectroscopy.

The surface of the ribbon-shaped Fe (100) crystal of five-nine purity was cleaned by the repeated cycles of ultrahigh vacuum flashing, Ar⁺ ion bombardment and anneal at 500°C and the surface cleanliness was determined by means of Auger electron spectroscopy. The main contaminants (C, O and S) on the surface could be removed by painstaking long-time cleaning processes as described above. Finally, the atomically clean surface having p(1×1) LEED pattern and carbon concentration of less than 0.5 percent of a monolayer coverage could be prepared. The Fe (100) clean surface was maintained at less than 1×10^{-9} Torr during the measurement of the characteristic energy loss spectra by the aid of the sputter-ion pumps, and the partial pressures of the active residual gases in the system were monitored by the quadrupole mass filter. The characteristic energy loss spectra, mainly consisted of plasma loss peaks, were determined by the new method of electron spectroscopy originally developed by the authors.⁷⁾ In our new method of electron spectroscopy, a 2-grid LEED system with a transparent glass fluorescent screen was used as a retarding field electron energy analyzer. The reflected electrons from the surface were converted to photons at the fluorescent screen held at a positive potential of 3 KV and the emitted light was then detected by a photoelectron multiplier located outside a viewing window of the apparatus. The energy loss spectra in the first and second derivative forms were obtained, through the photomultiplier output, by the conventional potential-modulation-differentiation technique. The characteristic energy loss spectra of the Fe (100)p(1×1) clean surface having no detectable contaminants are shown in Fig. 1 (A) in the form of the second derivative. In Fig. 1 (A), the peaks denoted by (a) and (b) are believed to be due to the surface plasma and bulk plasma losses respectively, and their energy loss values were not varied by the change in incident electron energies in the range from 80 to 600 eV. The last peak denoted by (c) is presumably due to the double excitation of surface and bulk plasmons, but its energy value is considerably deviated from the summation of surface and bulk plasmon energy values. The comparison between present results and the past experimental results on the characteristic energy losses in Fe crystals is shown in Table I. In Table I, it can be seen that the energy loss values due to the bulk plasma excitation only are in fairly good agreement with each other, but the other energy loss values show marked scattering probably ascribed to the difference in sample structure, purity, surface cleanliness and the method used. Even in the case of the bulk plasma loss values including our results, the observed values of about 21 eV are markedly lower than the theoretical value, 31 eV, calculated by assuming all electrons outside the appropriate closed shell are free, namely 8 free electrons per Fe atom. In this type of transition

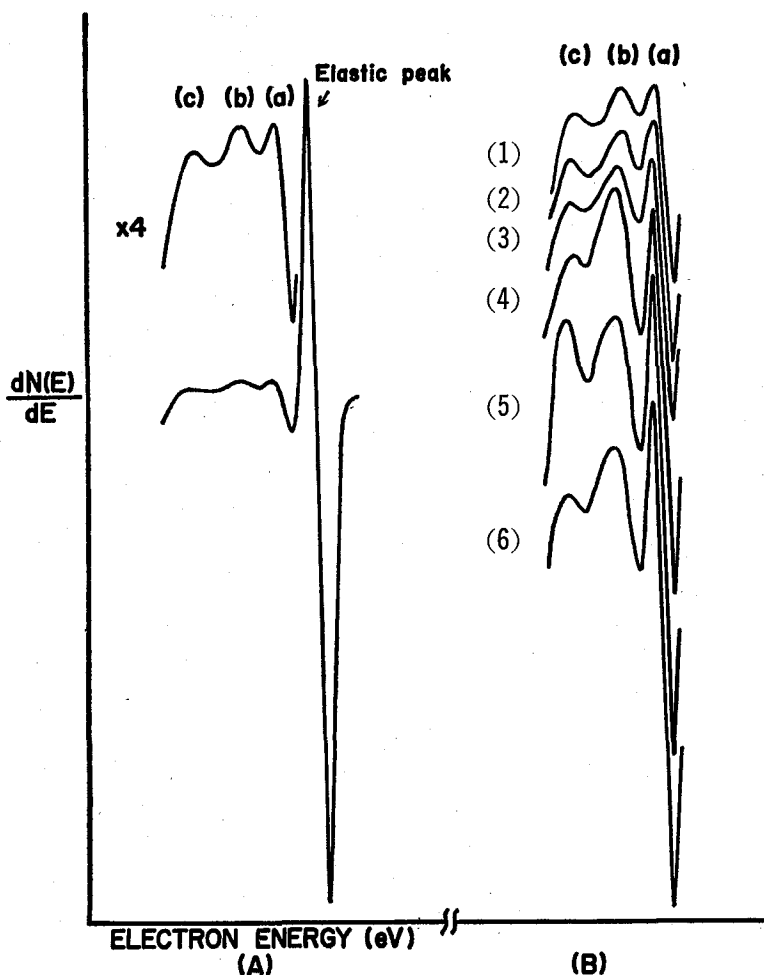


Fig. 1 (A) Plasma loss spectra of Fe(100)p(1×1) clean surface in the form of second derivative.

(a) surface plasma loss peak ($\Delta E=11$ eV)

(b) bulk plasma loss peak (21.5 eV)

(c) double excitation peak (36.5 eV)

incident electron energy: 98 eV

incident angle: 60° from surface normal

Fig. 1 (B) Variation of plasma loss peaks of Fe(100)c(2×2)-S surface as a function of sulfur coverage.

(a) surface plasma loss peak (b) bulk plasma loss peak

(c) double excitation loss peak

(1) Fe (100) clean surface (2) H₂S exposure at 650° C: 1 L

(3) 5 L (4) 20 L (5) 40 L (6) 100 L

metals there are so many electrons outside the closed shell that the simple concepts on the excitation of the free electron plasma oscillation cannot be applied. Furthermore, the relation between bulk plasmon and surface plasmon energy values for the clean Fe (100) surface obtained by the present work is still unsatisfactory because the relation,

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Table I. Characteristic Energy Losses in Fe Crystals.

source	surface plasma loss (eV)	bulk plasma loss (eV)	other losses	Fe sample form
Ref. 4)	16	20	56	metallic thin film
Ref. 5)	6	22	37 56	
Ref. 6)		24	48	
present work	11	21.5	36.5	Fe (100) clean surface
theoretical	21.9	31		

$\omega_s = \omega_p / \sqrt{2}$ does not apply, where ω_s and ω_p are surface plasma and bulk plasma frequencies, respectively. Finally, we would like to mention that the more detailed investigations with the aid of high resolution electron spectroscopy are necessary to reveal the fine structure of energy loss spectra which cannot be obtained by our present method using retarding field technique of inferior resolution.

To obtain the further information on the influence of the presence of adsorbed atoms on the loss spectrum, the variation of the loss spectrum as a function of the sulfur coverage under well-defined controlled conditions has been investigated in some detail. When the Fe (100)p(1×1) clean surface was heated at about 600°C after adsorption or during the admission of H₂S, the Fe (100)c(2×2)-S structure was formed by the decomposition of H₂S on the surface and this structure was completed two-dimensionally at H₂S exposures from 1 to 2 Langmuir, showing no change both in LEED pattern and the (1/2, 1/2) LEED spot intensity by further exposures, while the 150 eV sulfur Auger peak height was increased successively with the H₂S exposure up to 30 L as shown in Fig. 2 (A), (B). These results would indicate the surface-to-bulk diffusion of sulfur atoms or, in other words, the bulk-to-surface diffusion of Fe ions at elevated temperatures during the exposure to H₂S at about 10⁻⁷ Torr. In the case of the Fe(100)c(2×2)-S structure produced at less than 2 L exposure, the location of sulfur atoms is considered to be limited within the first atomic layer (presumably reconstructed), hence the influence of the sulfur adatoms on the plasma loss spectrum might be negligibly small in this case. In Fig. 1 (B), the variation of the plasma loss spectrum as a function of the sulfur coverage formed by H₂S exposures from 1 to 100 L, is shown sequentially in the second derivative form. It can be seen from these results that the intensity increase of surface and bulk plasma loss peaks by the growth of pseudo-sulfide layers on the Fe (100) surface, was unexpectedly large in comparison with the energy shifts of loss peaks which are summarized in Table II. As regards the energy

Table II. Energy Shift of Plasma Loss Peaks as a Function of H₂S Exposure at 650°C.

surface condition	surface plasma loss (eV)	bulk plasma loss (eV)	double excitation loss (eV)
clean surface	11	21.5	36.5
H ₂ S exposure at 650°C (5 L)	11.5	21.5	37
H ₂ S exposure at 650°C (100 L)	12	22.5	39

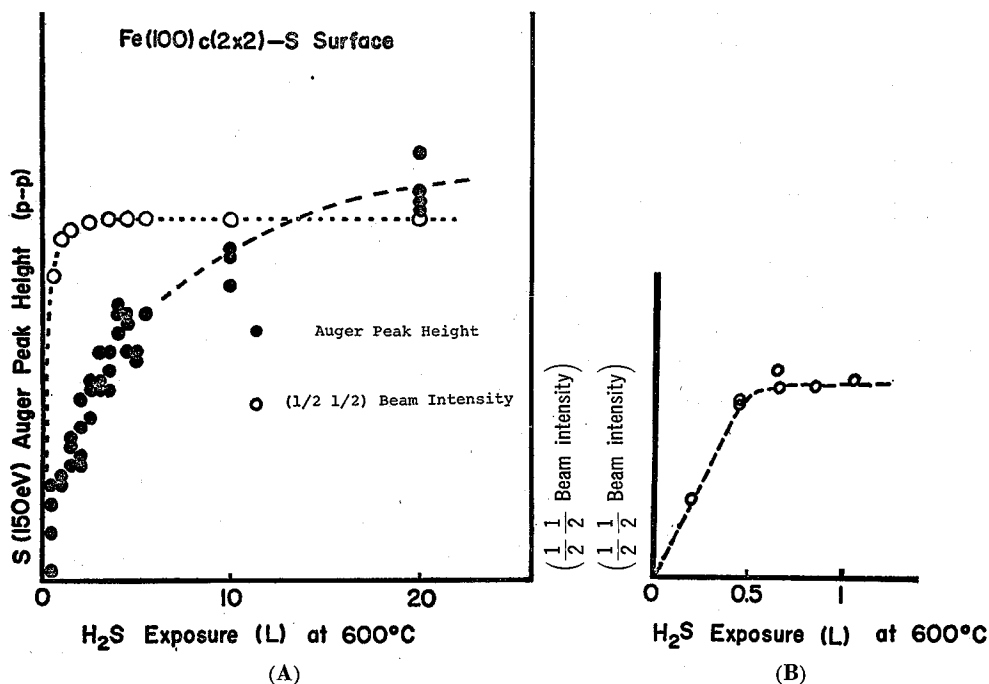


Fig. 2 (A) Intensity change of $(1/2, 1/2)$ LEED beam and sulfur Auger peak height both as a function of sulfur coverage.

Fig. 2 (B) Detailed intensity change of $(1/2, 1/2)$ LEED beam from $\text{Fe}(100)c(2 \times 2)\text{-S}$ surface as a function of sulfur coverage.

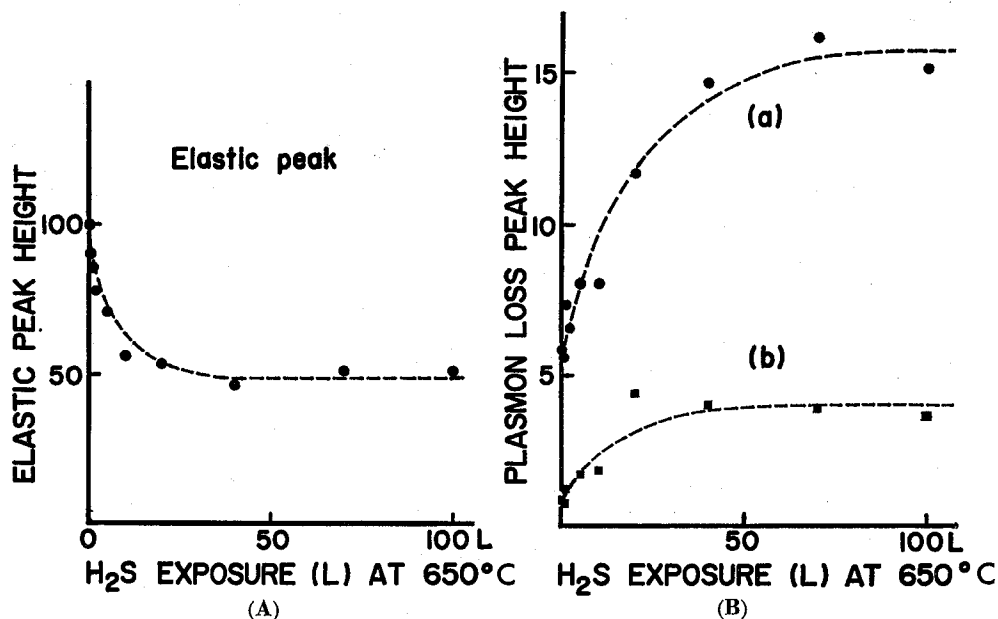


Fig. 3 (A) Elastic peak height from $\text{Fe}(100)$ surface as a function of sulfur coverage.

Fig. 3 (B) Plasma loss peak height from $\text{Fe}(100)$ surface as a function of sulfur coverage. (a) surface plasma loss peak (b) bulk plasma loss peak.

shift of the surface plasma loss peak by the sorption of sulfur atoms, the shift of only 1 eV after 100 L exposure at elevated temperatures is extraordinarily small against expectation in which the considerable energy shift can be anticipated because several tens of pseudo-sulfide layers are believed to be developed on the Fe(100) surface, after 100 L exposure at elevated temperatures, from the results obtained by Auger electron spectroscopy as already shown in Fig. 2 (A). The intensity changes of the elastic peak and the plasma loss peaks as a function of the sulfur coverage are respectively depicted in Figs 3 (A) and (B), where the intensity change of the three peaks seems to have a definite trends to reach saturation, at the H₂S exposure of about 50 L, probably due to the short penetration depth of low energy incident electrons of about 100 eV. The interpretation of very large intensity increase of the surface and bulk plasma losses by the presence of sorbed atoms as revealed by the present work is far beyond the theoretical approach at present, therefore, the accumulation of the accurate experimental results for the well-defined solid surfaces by means of combined LEED, Auger and related electron spectroscopies should be necessary as a first stage of the new development.

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