# Low-energy electron transmission experiments on graphite

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Low-energy-electron transmission (LEET) spectra were measured for graphite using electron energies below 30 eV. The observed LEET spectra have broadened square-wave-like features, and comparison with the conduction-band density of states above the vacuum level measured by ultraviolet photoemission and inverse photoemission spectroscopies indicated that the conduction-band density of states was not observed in the LEET spectra except band gaps. It is concluded that band gaps are more strongly reflected in LEET spectra than other features in the density-of-states. It is expected that electron-interference effects along the surface normal dominate LEET features, even for a very thick sample, where the energy dependence of electron-transmission probability through a one-dimensional periodic potential along the surface normal does not reflect the variation of the density of states (except band gaps).

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## I. INTRODUCTION

Low-energy-electron transmission (LEET) has been shown to be sensitive to crystalline order and to the electronic band structure in the direction of beam incidence.[1,2] Attempts have been made to correlate LEET spectra with the conduction-band density of states (CB-DOS) above vacuum level.[3–15] For example, Plenkiewicz *et al.*[5] argued from theoretical consideration on electron-transmission phenomena in a quasielastic regime, that LEET spectra can be expressed by the CB-DOS with some modification by the energy-dependent electron mean free path, and showed a fare agreement between theoretical CB-DOS and that deduced from observed LEET spectra for solid xenon films. They also showed that LEET features are closely related to the CB-DOS variation for solid-argon films.[7,9] Furthermore, Caron *et al.*[14] touched upon the correlation between the LEET features and the one-dimensional CB-DOS for platinum ribbon with preferentially [111] oriented crystallites. These results have been basically obtained by a theoretical analysis of the LEET spectra, and the theoretical model was based on an idea that the injected electron current through the surface barrier is proportional to the CB-DOS of a target for the elastic-scattering regime.[5,7–9] From fully experimental point of view, a direct experimental correlation between LEET maxima and the high CB-DOS parts was pointed out for thin films of *n*-alkane.[6] In the target-current measurements during angle-resolved inverse photoemission spectroscopy (ARIPES) of graphite, Schäfer, Schlüter, and Skibowski[16] observed remarkable current modulation, and they discussed the origin of the current modulation observed at normal-incidence condition using the CB dispersion parallel to the *c* axis in $\Gamma$-*A* direction.

Michaud and co-workers[17,18] demonstrated using energy-tuned high-resolution electron-energy-loss spectroscopy that the incidence-energy dependencies of the quasielastic and inelastic electron intensities have one-to-one correspondence with the CB-DOS for electrons backscattered to various directions. These results seem to suggest that LEET spectrum also reflects the CB-DOS through inelastic scattering of incidence electrons.

On the other hand, it has been also shown for very thin films deposited on conductive substrates that a quantum interference of an injected electron between two interfaces, film-vacuum and film-substrate interfaces, is reflected in LEET.[19–21] This has been considered to be a different category of phenomena from that where the CB-DOS is reflected in LEET.

Based on these many works, it is commonly understood that main LEET features observed for thick films are ''related'' to the CB-DOS.[1,2] In earlier low-energy-reflection experiments on (111) surfaces of fcc metals, however, Jaklevic and Davis[22] pointed out that no correspondence can be seen between the reflection spectra that are correlated with LEET spectra and the CB-DOS except band gaps.

Although we can be convinced that the band gaps existing along the surface normal appear as clear minima of LEET spectra as the result of electron reflection at the surface, it is not straightforward to understand that LEET maxima reflect peaks in the CB-DOS. The latter is because (i) most of LEET experiments, which intended to show that LEET spectrum reflects the variation of the CB-DOS, were performed for polycrystalline specimens with various crystal orientations, (ii) discussion was made by comparison between experimental results and theoretical CB-DOS, and (iii) the theoretical model of LEET was based on an assumption[5,7–9] that the electron-injection probability through the surface barrier is proportional to the CB-DOS. In polycrystalline systems, many band gaps may exist along the surface normal due to various orientations of crystallites, and thus there is a possibility that experimental LEET maxima happen to appear at energy positions between adjacent gaps, where nonzero values of the CB-DOS exist. In this case, the LEET maxima do not necessarily reflect peaks of the CB-DOS. Furthermore, it is, in general, not so easy to obtain an accurate CB-DOS by theoretical calculations. For better understanding of the correlation between LEET features and the CB-DOS variation, therefore, it is desirable to compare LEET features with the CB-DOS structure observed by other CB spectroscopies.

 

In order to evaluate the correlation between LEET features and the CB-DOS or to clarify an origin of main LEET features experimentally, we measured LEET and ultraviolet photoelectron spectra (UPS) of a cleaved surface of graphite. Graphite shows a clear variation of the CB-DOS that was experimentally observed in secondary-electron region of (UPS),[23–25] secondary-electron-emission spectra,[26] and ARIPES.[16,27] The present results indicate that LEET maxima are not related to CB-DOS peaks observed by other methods, and only LEET minima coincide with the band gaps. Furthermore, it is pointed out that the electron-transmission probability through a one-dimensional potential array along the surface normal, which does not essentially reflect the CB-DOS, seems to be reflected in the LEET.

## II. EXPERIMENT

The highly oriented pyrolytic graphite (HOPG, Union Carbide) samples, that consist of oriented polycrystal with the basal planes parallel to the surface, were *in situ* cleaned by heating typically at 670 K for 13 h in the preparation chamber, and their LEET and He I UPS were measured at a vacuum condition of $10^{-9}$–$10^{-10}$ Torr. Thickness of the cleaved samples was about 1 mm. In the LEET experiments, the incident electron beam was normal to the sample surface, and the incidence current $I_i$ was kept at $3\times10^{-11}$ A, independent of the incident electron energy $E_i$. The LEET measurements were carried out using a spectrometer described elsewhere,[28] and the He I UPS were measured using the apparatus described in Ref. 29.

The energy resolution was better than 0.4 eV for LEET spectra as estimated from the injection-peak width at $E_i = 0$ eV in the first derivative of the spectra, and 0.3 eV for UPS from the observed Fermi edge of an evaporated gold film.

## III. RESULTS AND DISCUSSION

Figure 1 shows LEET and He I UPS of HOPG, where ARIPES of graphite measured along the surface normal by Schäfer, Schlüter, and Skibowski[16] is compared. In the UPS, a sharp peak $X$ and a shoulder $X'$ are seen at the kinetic energy of about 3 eV with an energy separation of ~0.8 eV in the secondary-electron region, as reported previously.[23–26] Their kinetic-energy positions are independent of the incident photon energy, and they have been already ascribed to scattered electrons accumulated in the high CD-DOS parts ($\Gamma_5^+$,$\Gamma_6^-$) that originate from $\sigma^*$ conduction bands.[23–26] Although these CB-DOS peaks were not observed in the ARIPES, the reason is still controversial.[16] The other features seen at larger kinetic energies in the UPS are due to valence bands.[23,24] The LEET spectrum has two rectangle like features in this energy range, and we could not detect any LEET features, which correlate to the $\sigma^*$ CB-DOS features even in the second derivative of the spectra. Furthermore, when we compare the LEET spectrum with the ARIPES,[16] which reflects the CB-DOS along the surface normal, we cannot see any traces in the LEET spectrum that correspond to the prominent CB-DOS peaks ($A$, $B$ and $C$) in

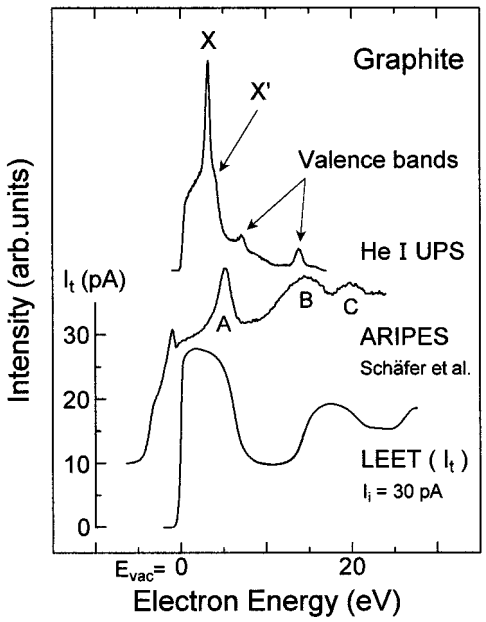


FIG. 1. LEET spectra and He I UPS of graphtie (HOPG). Normal-incidence ARIPES (Ref. 16) of HOPG is compared.

the ARIPES above the vacuum level. If sharp CB-DOS peaks $X$, $X'$, and $A$ were reflected in the LEET spectrum, they should be detected separately, since energy separations between peaks $X$, $X'$, and $A$ are ~0.8 eV for peaks $X$ and $X'$, and ~1.1 eV for $X'$ and $A$, each of which is larger enough than the experimental energy resolution. These results lead to a conclusion that main LEET features do not reflect any peaks in the CB-DOS, which were observed in other CB-DOS spectroscopies. Furthermore, it is interesting to notice that CB-DOS peaks in the ARIPES are located at both sides of each rectanglelike LEET feature.

These somewhat confusing results led us to compare an idealized electron-transmission-probability spectrum for the simplest one-dimensional potential system with the corresponding CB-DOS and with the observed LEET in order to see what is happening in LEET. For this, we first compared the CB-DOS and an electron-transmission-probability spectrum computed for a one-dimensional square-well potential array with constant inner potential $V_0$ shown in Fig. 2 (upper panel). The computations were performed for $V_0=-3$ eV, $V_1=-23$ eV, $a=0.6$ Å, and $b=2.75$ Å, where $a+b=3.35$ Å was selected to correlate the interplanar distance of graphite. The number of the square-well potentials $n$ was 1000 for the computation of transmission-probability spectra with two values of phenomenological electron attenuation length $\lambda=\infty$ and 30Å, and $n=100\,000$ for the DOS. Here $n$ is not important when it is enough large. Although the model seems to be too simple and too crude, it is worth understanding the correlation between features in the transmission-probability spectrum and the CB-DOS. The computed CB-DOS and electron-transmission-probability spectra are compared in Fig. 2. In the computed one-dimensional CB-DOS, as is well known, sharp DOS peaks appear at the band edges. The transmission probability spectra for $\lambda=\infty$ and 30

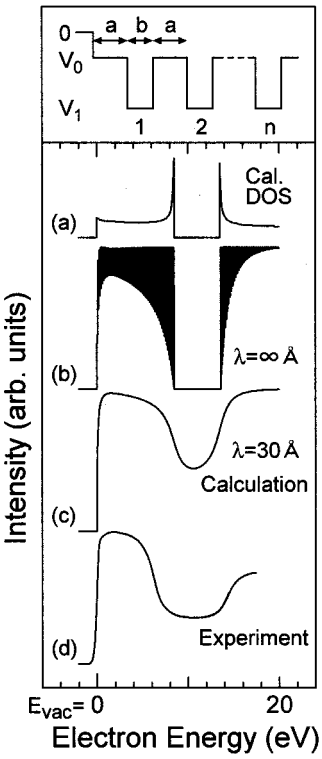


FIG. 2. Comparison between computed density-of-states (DOS) above vacuum level (a) and electron-transmission probability spectra [(b) and (c)] for an idealized one-dimensional square-well potential array. The experimental LEET on graphite (d) is also compared. In the upper panel, the one-dimensional potential used in the model computations is shown. The computations were performed for $V_0=-3$ eV, $V_1=-23$ eV, $a=0.6$ Å, and $b=2.75$ Å, where $a+b=3.35$ Å was selected to correlate the interplanar distance of graphite. The number of the square-well potentials ($n$) was 1000 for the computation of transmission-probability spectra with two values of phenomenological electron attenuation length $\lambda=\infty$ and 30 Å, and $n=100\,000$ for the DOS. The electron-energy dependencies of the potential structure, electron effective mass, and $\lambda$ were fully neglected in the model computations.

Å are shown in Figs. 2(b) and 2(c), respectively. In the result with $\lambda=\infty$, the value of the transmission probability is zero in the band-gap regions and oscillates in the band regions depending on the number of square-well potentials used. This oscillation is not resolved in Fig. 2(b), but can be recognized as the black area due to the fine oscillation. The spectrum after smoothing these fine oscillations using Gaussian function with a finite energy width does not have peaks at the band edges, where CB-DOS peaks exist, and shows only a square-wave-like curve reflecting the band and band-gap regions (not shown). This is because the value of the transmission probability at the dip of each fine oscillation becomes smaller by approaching the band edge and is about unity at the peak of each oscillation with a small modulation due to the existence of $V_0$, although the number of the fine oscillations per unit energy width increases with the CB-DOS. For $\lambda=30$ Å, a broadened square-wave-like curve is obtained without peaks corresponding to the CB-DOS spikes. The important point that we can confirm from this comparison is that prominent electron-transmission phenomenon is observed only for the energy regions where the CB-DOS is not zero, and the variation of the CB-DOS for the energy regions of the nonzero CB-DOS is not reflected in the transmission-probability spectrum. Furthermore, when we introduce a finite $\lambda$ to dump the electron wave function, the fine oscillation disappears and only a diffused square-wave-like structure is seen, where only the band gaps appear as dip features. These results indicate that LEET does not reflect the CB-DOS variation except band gaps, and this characteristic is essentially similar to that of light transmission through a photonic crystal, where the DOS of photonic bands is not reflected in the light-transmission spectrum except band gaps.[32,33]

Here, we compare the computed LEET with the observed one. In this comparison, we must remember that the above computation was carried out by neglecting energy dependencies of the electron effective mass $m^*$, $V_0$, and $V_i$, and such a situation may not be adopted for an actual crystal of graphite. Therefore, the comparison was performed for a narrow energy region as shown in Fig. 2. The computed spectrum shows a surprisingly meaningful correspondence with the observed LEET spectrum of HOPG, although we used the simplest one-dimensional square-well potential array and neglected the electron-energy dependencies of potentials, the electron inelastic scattering, and ejection of valence electrons, etc. In passing, when we introduce energy-dependent potentials ($V_0$ and $V_i$) or energy-dependent $m^*$ as an adjustable parameter, the observed LEET curve can be reproduced for wider energy regions. Important physics obtained from this simple comparison and from the present experimental evidence that the CB-DOS peaks were not detected in the LEET, is that variation of CB-DOS is not reflected in the electron transmission except band gaps. Such results indicate that when the inelastic electron scattering is not dominant, the electron interference in the periodic potential is mainly reflected in a LEET spectrum even for very thick sample and it does not reflect the CB-DOS, but only band gaps. This means that the electron-interference effect strongly contributes to LEET features even for a very thick sample if it is a well-ordered crystal.

Although importance of three-dimensional role in LEET was pointed out by Naaman and his coworkers for films with many defects or disorder,[1,30,31] the present result suggests that main LEET features in a well-ordered system are dominated by the band-gap reflection and the interference of injected electrons along a one-dimensional potential array along surface normal, and therefore they do not reflect the CB-DOS explicitly except the zero value of it, namely band gaps. An evidence of such interference effects were also observed in well-ordered organic layers of large organic molecules.[34]

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