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Experimental observation of microscopic optical surface phonon: TaC(100)

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Microscopic optical surface phonons have been observed experimentally on the clean TaC(100) surface. The nature of the vibrational mode is studied using high-resolution electron energy-loss spectroscopy.

Microscopic optical surface phonons, with vibrational energies located in the energy gap between the optical and the acoustical bulk phonon bands and hence with amplitudes of vibration localized within a few atomic layers near the surface, was first predicted by Lucas¹ and Wallis, Mills, and Maradudin² in 1968. Then, Tong and Maradudin³ investigated the properties of microscopic optical and acoustical surface phonons throughout the two-dimensional Brillouin zone of ionic crystals. In the seventies, Chen and his co-workers⁴ performed more refined calculations for the (100) surface of several alkali halides. Those studies provided not only fundamental knowledge on surface phonons, but also insight into new phenomena such as surface superconductivity.⁵

In contrast to the theoretical efforts, only little experimental work has been done on this subject. Only comparative measurements of some physical quantities on bulk samples and microscopic crystals can be found in the literature.⁶ Inelastic atomic scattering and high-resolution electron-energy-loss spectroscopy (EELS) are the most suitable techniques for investigating surface phonons. At present, however, the observable energy using inelastic atomic scattering is restricted to the acoustical phonon region.⁷ In addition, EELS studies have not yet succeeded in observing microscopic optical surface phonons. This is presumably due to material problems.⁸

In this paper, we report the first experimental observation of optical phonons reflecting truly microscopic surface properties. The specimen used in this study, the TaC(100) surface, was carefully selected for the following reasons: (i) Since the V_a -group transition-metal carbides including TaC are metallic compounds, the conduction electrons eliminate the long-range component of the Coulomb interaction, which is the origin of the troublesome Fuchs-Kliever (FK) wave,⁹ hence no FK wave is expected to be excited by electrons.¹⁰ (ii) TaC has a rocksalt crystal structure, for which the (100) surface has been widely studied theoretically. (iii) The energy gap of TaC between the optical and acoustical phonon bands is largest among the V_a -group transition-metal carbides. Hence the soft optical modes at the surface have a high probability of falling into the energy gap.

In this study, evidence for microscopic optical surface

phonons was provided by the following observations: (i) The observed vibrational mode is extremely sensitive to microscopic surface change. (ii) Its vibrational energy appears in the gap between the optical and acoustical bulk phonon bands. In the angle-resolved EELS spectra, in addition, the following properties were seen: (i) The atomic displacement of this mode in the long wavelength limit has a component perpendicular to the surface. (ii) The dispersion relation of the mode is found to be small (< 2 meV), which is what is expected for an optical surface phonon polarized perpendicularly to the surface.^{2,5}

The clean TaC(100) surface, being a neutral surface with an alternating array of Ta and C, has a 1×1 atomic structure as revealed by low-energy electron diffraction (LEED). After a cleaning procedure of flash heatings up to 1900 K under ultrahigh vacuum conditions of 10^{-10} torr, no impurities could be detected within the limit of the ion-scattering spectroscopy (ISS) sensitivity (~ 0.01 monolayer). In the EELS spectra, however, traces of impurities (~ 0.005 monolayer) appeared during the measurement. The electron spectrometer used in this EELS apparatus employed an advanced version of a double-pass cylindrical selector as the energy-dispersing elements.¹¹ By optimizing the deflection angle of the selector, a high resolution of 2.9 meV was established at the normal sample current of 10^{-10} A.¹² Angle-resolved EELS spectra were obtained by rotating an incident beam around the specimen within the $(0\bar{1}1)$ plane as illustrated in Fig. 1(b).

Figure 1(a) shows a typical EELS spectrum of the clean TaC(100) surface. It shows a characteristic loss feature at a vibrational energy of 57.4 meV. This phonon loss was found to be extremely sensitive to surface contamination. The spectrum (a) was therefore measured immediately after flashing (~ 1900 K) with the sample temperature above room temperature; an average value of 600 K was roughly estimated from the ratio of the intensity of the gain peak at -57.4 meV to the loss peak. Typical recording times for the spectra were ~ 8 min. The extra loss peaks in spectrum (a) originate from a small amount of chemisorbed residual gases with a coverage of $\Theta \sim 0.005$ monolayer. They are assigned in Fig. 1(a).

During oxygen chemisorption, the intensity of the charac-

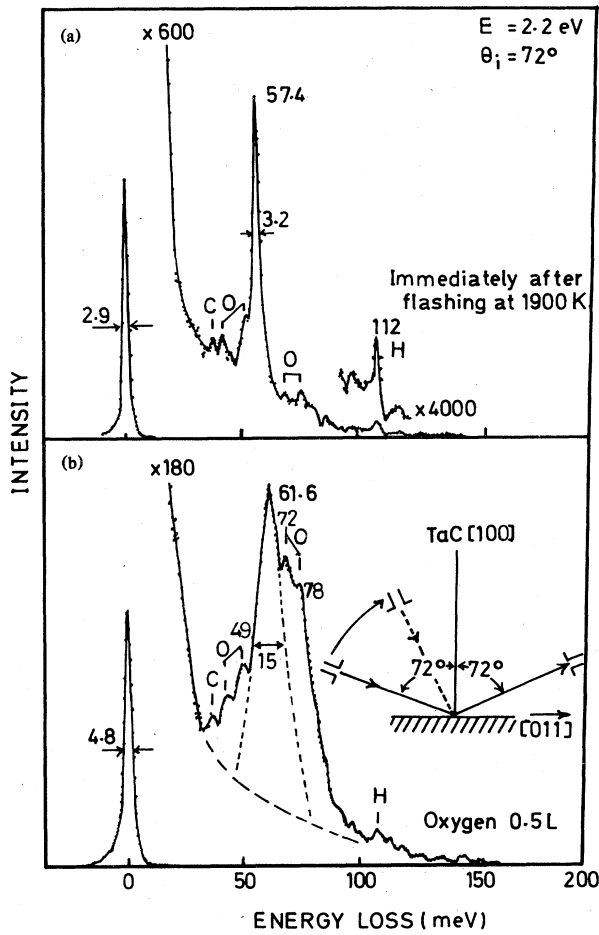


FIG. 1. Typical EELS spectra of the TaC(100) surface measured in the specular direction (a) immediately after flashings up to 1900 K and (b) after the specimen was exposed to 0.5 L of oxygen at room temperature. The scattering geometry of the angle-resolved EELS is illustrated in (b). The incident electrons were injected along the [011] crystal direction, and rotated within the (0 $\bar{1}$ 1) plane, while the scattering angle is fixed at 72° from normal to surface.

teristic loss (57.4 meV) decreased. Instead, a new peak appeared at 61.6 meV as shown in Fig. 1(b). The broad peak at 61.6 meV in spectrum (b) consists of two peaks; i.e., the characteristic loss at 57.4 meV is embedded in the broad peak. Some extra loss peaks due to oxygen chemisorption appear at energies above and below that of the broad peak in spectrum (b). From their vibrational frequencies, together with the intensity changes due to oxygen chemisorption and desorption, we have deduced the origin of these losses. They originate from oxygen chemisorbed at the bridge site of the Ta atoms (78 meV), at the site bound to both two Ta atoms and one carbon atom (72 meV), at the fourfold hollow site (49 meV) and from the optical surface phonon of the oxygen-covered surface (61.6 meV). Detailed discussion will be published in near future.

More evidence for the microscopic character of the phonon loss was provided by the observation of another crystallographic surface; no similar loss was found on the clean (111) polar surface, of which the topmost layer consists of metal atoms.

These properties are much similar to those of the surface phonon localized at microscopic steps on the clean Pt[6(111) \times (111)] surface.¹³ On the TaC(100) surface, however, no surface defects such as steps and atomic vacancies were found by preliminary ICISS (impact-collision ion-scattering spectroscopy) measurements, which is the most powerful method to detect them.¹⁴ Therefore interpretation of the vibrational mode as being localized at surface defects has not been verified.

Angle-resolved EELS spectra give us additional information about the vibrational mode. The angular distribution of the loss intensity shows a very sharp peak in the specular direction, which is the characteristic feature of dipole scattering. The phonon loss is therefore caused near the center of the two-dimensional Brillouin zone, and its atomic displacement has its dynamic dipole moment perpendicular to the surface. Therefore, the observed loss can be assigned to the S_2 mode discussed by Chen, Aldrege, de Wette, and Allen⁴ and Benedek, Miura, Kress, and Bilz,⁵ because the other optical modes (Lucas modes), S_4 and S_5 , have horizontal polarization in the long wavelength limit.

The dispersion curve of the phonon loss was also obtained from the angle-resolved EELS spectra using momentum conservation parallel to the surface. The data points are indicated by the open circles in Fig. 2. The measured region in Fig. 2 was limited to almost half of the Brillouin zone, because the counting rate of the signal became extremely low beyond the half-point, and hence no reliable

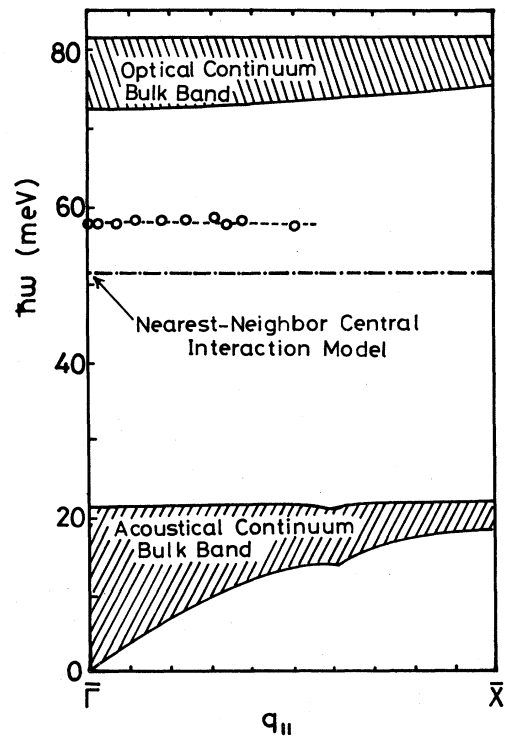


FIG. 2. Experimental dispersion curve in the symmetry axis from Γ to \bar{X} of the TaC(100) surface. The open circles represent the data points. The dash-dotted line represents the vibrational energy of localized vibration calculated from the model of a linear diatomic chain with a free end. The crosshatched region indicates the energy bands allotted to the bulk phonons (Ref. 17).

measurement could be performed there in this work. The small dispersion (< 2 meV) observed in Fig. 2 is understood with the help of a simple model with nearest-neighbor central interactions. By neglecting the angle-bending interaction, the dynamic equation of a semi-infinite crystal lattice with a rocksalt structure can be reduced to three independent equations; two of them express the dynamic motion of atoms parallel to the surface, and they are easily solved with periodic boundary conditions. The other equation represents motion perpendicular to the surface; this dynamic equation is the same as the model of a linear diatomic chain with a free end, and its solution is given by Wallis.¹⁵ In his calculation, localized vibrations exist near the one end, if the end atom is the lighter one; the vibrational energy of the localized mode appears in the energy gap between two bulk phonon bands. Similar to the Lucas modes, it comes from the surface softening of the LO (longitudinal optical) bulk mode due to perturbation of the chemical bonds. The vibrational energy is found to be $\hbar\omega_0/\sqrt{2}$, if we assume that the force constant of the end atom k_0 is the same as in the bulk. Here ω_0 is the vibrational frequency of optical phonons in the long wavelength limit, $\omega_0 = \sqrt{2k_0/\mu}/2\pi$, and μ is the reduced mass.

Since the localized vibrations do not couple with the other mode with horizontal polarization in this approximation, there is no dispersion against the parallel crystal momentum

q_{\parallel} as indicated by the dash-dotted line in Fig. 2. Advanced calculations including the second and third nearest-neighbor interactions indicate small dispersion in this S_2 mode.^{2,5}

The difference between the observed energy and the calculated one is attributed to the oversimplification of the model; generally speaking, the force constant of the end atoms is different from that in the bulk. If the force constant which couples atoms in the first layer to those in the second is increased by 17%, then good coincidence is obtained. But this correction for the force constant strongly depends on the model. If the second and third nearest-neighbor interactions are included in the calculation, the agreement is expected to be much improved without a large change in the force constant.⁵ Hence further theoretical work is required so as to determine the precise value of the force constant of the end atoms.

Finally, we note the other optical surface phonons, namely, the Lucas modes. Since the Lucas modes have a polarization parallel to the surface in the long wavelength limit, they are observed only in the impact scattering regime, similarly to the acoustical surface phonon reported recently by Lehwald *et al.*¹⁶ In the impact scattering measurement of this work, we observed also a small feature at the vibrational energy just below the TO bulk phonon, corresponding to the Lucas modes, and improved measurements throughout the two-dimensional Brillouin zone are now in progress.

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scopic optical surface phonon discussed here, so that the feature of the microscopic optical phonon in the EELS spectra might be embedded in the high background of the large loss of the FK wave.

⁹See Ref. 8.

¹⁰In fact, recent theoretical work has shown no FK mode on the (100) surface of similar metallic compounds, TiN. See Ref. 5.

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