Hot-electron relaxation in the layered semiconductor $2H$-MoS_2 studied by time-resolved two-photon photoemission spectroscopy

Akinori Tanaka*
Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627
and Department of Physics, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan

Neil J. Watkins and Yongli Gao
Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627
(Received 10 May 2002; revised manuscript received 19 September 2002; published 24 March 2003)

We have carried out a femtosecond two-photon photoemission study of layered semiconductor $2H$-$MoS_2(0001)$ surface. From the detailed time-resolved two-photon photoemission measurements as a function of electron excitation energy, it is found that the relaxation lifetime of hot-electron is extremely short ($\leqslant$60 fs) and the inverse lifetime depends linearly on the excess energy above the conduction-band minimum. Deviation from the Fermi liquid behavior in layered semiconductor $2H$-MoS_2 is discussed.

DOI: 10.1103/PhysRevB.67.113315 PACS number(s): 78.47.+p, 79.60.−i

The transient dynamics of hot electrons created by photoexcitation are attracting much interest, since the hot-electron dynamics plays an important role in the various physical and chemical phenomena in the condensed matter. The excited hot electrons relax through a number of decay processes, such as electron-electron scattering, electron-phonon scattering, electron-impurity/defect scattering, and scattering with other elementary excitations.[1] The detailed understanding of hot-electron dynamics will provide not only information about the fundamental interactions in the many-body systems but also knowledge of the physical and chemical surface processes including the surface phase transition, adsorption, desorption, catalysis, and electrochemical reaction. Especially from the viewpoint of both fundamental and device physics, the hot-electron dynamics in semiconductor systems is a very important issue. Up to now, the excited-electron dynamics in semiconductors has been studied extensively by optical spectroscopic methods on femtosecond time scales with the development of ultrafast pulse lasers. On the other hand, among the time-resolved spectroscopic methods, time-resolved two-phonon photoemission (TR-2PPE) spectroscopy is a unique method to observe directly the temporal evolution of excited electrons within the conduction band that may not be easily accessible through optical techniques.[2] Therefore, TR-2PPE spectroscopy is an effective method to study the excited-electron dynamics over a much broader range of electron densities. In this work, we have carried out a femtosecond TR-2PPE study of $2H$-MoS_2 as a prototype layered semiconductor. TR-2PPE spectroscopy has been used to study the hot-electron dynamics on noble and transition metals and semiconductors by several researchers.[2–9] The present work elucidates the fundamental properties associated with the highly excited-electrons in two-dimensional layered semiconductors from the results of a TR-2PPE study on $2H$-MoS_2.

TR-2PPE measurements were performed with an ADES 500 (VG Mictrotech Co.) photoelectron spectrometer and a femtosecond self-mode locked Ti:sapphire laser (Tsunami, Spectra Physics Co.). A $2H$-MoS_2 single-crystal was cleaved *in situ* to obtain a clean (0001) surface. The cleanliness and structure of $2H$-$MoS_2(0001)$ surface were checked by x-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED) measurements. The cleaved surface of $2H$-MoS_2 shows no XPS signal from contaminants and exhibits a sharp 1×1 LEED pattern. The output of fundamental light from the Ti:sapphire laser has a pulse width of about 50 fs, pulse energy of about 9 nJ, wavelength of about 750 nm, and a repetition frequency of 82 MHz. The second harmonic light, with a photon energy of around 3.3 eV, was generated by using a 250-μm-thick beta barium borate doubling crystal (TP-1B Tripler, Uniwave Technology Co.), and a pair of external prisms was used for group velocity dispersion compensation of the frequency-doubled light. The frequency-doubled light was then split into two beams with equal intensities by a beam splitter. One beam was used as a pump pulse to generate the excited electron in the sample, while the other beam was used as a probe pulse to photoemit the excited electrons. After one of the beams was passed through the variable delay line, the two beams were recombined to make coaxial beams in order to obtain the both spatial and temporal overlap on the sample surface. The two beams were then cross polarized using a half-wave plate in order to eliminate coherent artifacts due to the coherent two-photon excitation.[9] The pulse width of the frequency-doubled light was about 80 fs and was obtained by deconvolution of a pump-probe scan (cross-correlation trace) of a transition-metal tantalum reference, in which the lifetime of the excited electron is negligible far above the Fermi level ($>$3.0 eV).[7] The total energy resolution was about 150 meV, and all measurements were performed at room temperature. In order to reduce the effects of stray fields and to extend the range of detection angle (that is, momentum) being collected, the sample was biased with -10 V.

Figure 1 shows the two-photon photoemission (2PPE) spectrum of the $2H$-MoS_2 measured with photon energy of 3.31 eV at zero pump-probe delay. As shown in Fig. 1, the observed 2PPE spectrum exhibits a broad feature. This broad feature indicates that a phonon assisted indirect transition contributes to the observed 2PPE spectrum in addition to

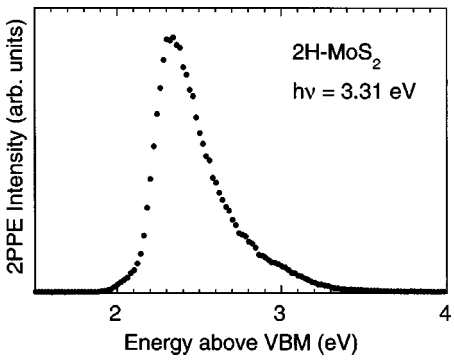

FIG. 1. Two-photon photoemission spectrum of $2H$-MoS_2 measured with a photon energy of 3.31 eV at zero pump-probe delay. The horizontal axis corresponds to the intermediate-state energy with respect to the valence-band maximum (VBM).

direct transition contributions.[10] From the band-structure calculation[11] and optical absorption spectra,[12] $2H$-MoS_2 is an indirect semiconductor with an indirect gap of 1.2 eV, in which the valence-band maximum (VBM) is located at the Γ point and the CBM is located in the middle of the Γ and K points in the Brillouin zone. From the comparison with the experimental ionization potential determined by the photoemission measurements with the He I resonance line ($h\nu = 21.2$ eV) for the same $2H$-$MoS_2(0001)$ surface, it is found that the high-energy cutoff and low-energy edge of the present 2PPE spectrum correspond to the 2PPE from the VBM and the cutoff due to the vacuum level, respectively. Therefore, from the measured kinetic energy of the photoelectron (E_k), the corresponding intermediate-state energy (E_i) can be determined by assuming the high-energy edge ($E_{k\,\max}$) in the 2PPE spectra as the highest intermediate-state, with one-photon energy ($h\nu$) above the VBM (E_{VBM}), i.e., $E_i - E_{\mathrm{VBM}} = E_k - E_{k\,\max} + h\nu$. As shown in Fig. 1, the intermediate-states observed in the 2PPE spectrum correspond to the energy region between 2.1 and 3.3 eV above VBM, that is, to an excess energy of about 0.9–2.1 eV above the CBM. In Fig. 1, there is no spectral intensity in the higher intermediate-state energy region beyond the high-energy edge of the 2PPE spectrum, indicating that there is no 2PPE from electronic states between the Fermi level and VBM. This means that there is no midgap state below the Fermi level in the present $2H$-MoS_2 samples.

TR-2PPE measurements were carried out by monitoring the number of photoelectrons at a given kinetic energy as a function of delay time between the pump and probe pulses. This pump-probe scan directly reflects the temporal evolution of the hot-electron population at a given intermediate-state. The present TR-2PPE spectra were measured with a pair of cross-polarized laser pulses. In this case, the temporal profile of the observed cross-correlation trace is described by the convolution of the autocorrelation function of the two laser pulses (Gaussian instrumental function) and the exponential decay function $\exp(-|t|/\tau)$ of the excited hot electron in the conduction band, where τ is the relaxation lifetime of the excited hot-electron.[9] Using this expression, we can derive the relaxation lifetimes of hot electrons at various electron excitation energies from the experimental cross-

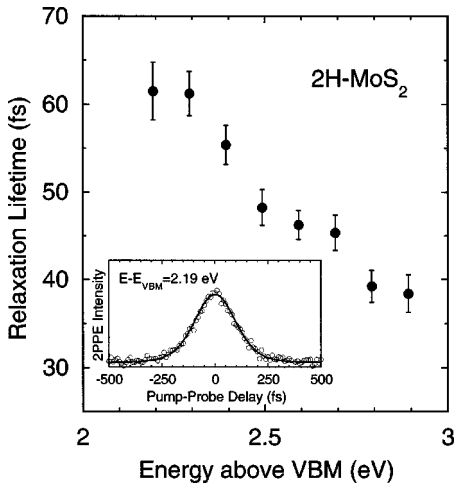

FIG. 2. Relaxation lifetime of excited hot-electron in the conduction band as a function of excited-electron energy relative to valence-band maximum (VBM) for $2H$-MoS_2. The inset shows the cross-correlation trace measured at the excited-electron energy of 2.19 eV above the VBM. Open circles and solid line show the experimental data and fits to the experimental data by the convolution of the exponential decay with the Gaussian instrumental function, respectively.

correlation traces. However, the population of an excited state might be refilled due to the energetic decay of excited electrons in energetically higher-lying states, building up a secondary electron cascade.[3–5,9] Therefore, the observed cross-correlation trace might be affected by this cascade effect, in fact, the deviations from the convoluted function of the simple exponential decay with the Gaussian instrumental functions have been observed in the cross-correlation traces.[3–5,9] This cascade effect definitely plays a more important role for the lower excited states. In the inset of Fig. 2, we show a cross-correlation trace at the excited-electron energy of 2.19 eV above VBM and the exponential fit to experimental results. As shown in the inset of Fig. 2, even at the lowest excited-electron energy in the present experiments, the observed cross-correlation trace is reproduced fairly well by the convoluted function of a single exponential decay function with the autocorrelation function of the two laser pulses. This means that the cascade effect is negligibly small in the present cross-correlation measurements for $2H$-MoS_2. Since the present measurements have been done for high excess energy region (higher than about 1 eV above CBM) and the observed relaxation lifetimes are very short (all below 65 fs as described latter in Fig. 2), the contribution from the cascade effect to the cross-correlation trace should be negligible. The transport of photoexcited electrons away from the photoelectron probing depth also makes significant contributions to the observed relaxation lifetime. However, this transport effect can be also neglected, since $2H$-MoS_2 has a two-dimensional layered structure. Therefore, the convolution of single exponential decay function with the autocorrelation function of the two laser pulses is adequate to describe the results of this experiment.

Figure 2 shows the measured relaxation lifetimes of hot electrons in the conduction band as a function of excited-

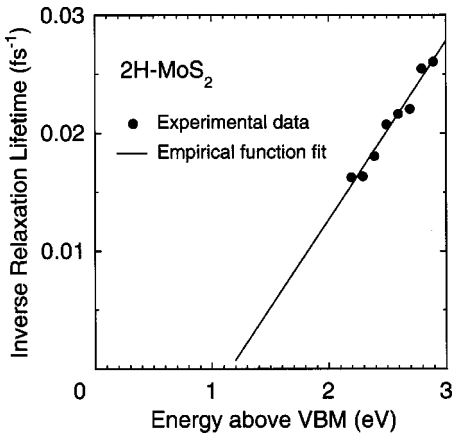

FIG. 3. Inverse relaxation lifetime (decay rate) of excited hot-electron in the conduction band as a function of excited-electron energy relative to valence-band maximum (VBM) for $2H$-MoS_2. Solid line shows the empirical function fit (see text).

electron energy relative to VBM. In general, the dominant process that determines the relaxation lifetime of hot electron on a femtosecond time scale is considered to be electron-electron interaction. For the ordinary interacting electron gas, Landau's theory of Fermi liquids has shown a quadratic dependence of electron-electron scattering rates on the electron excitation energy in both three- and two-dimensional (3D and 2D) electron gasses within logarithmic corrections.[13] As shown in Fig. 2, the experimental relaxation lifetime of hot-electron monotonously becomes faster with increasing electron excitation energy. This qualitative trend is consistent with the standard Fermi liquid picture, but this energy dependence seems to differ quantitatively.

In order to discuss the detailed excitation-energy dependence of the relaxation lifetime, we plot the inverse relaxation lifetimes (decay rates) versus the electron excitation energy above VBM in Fig. 3. In general, the electron-phonon scattering also significantly contributes to the hot-electron relaxation. However the contribution from electron-phonon scattering is independent of electron excitation energy in the measured energy region, since the Debye temperature of $2H$-MoS_2 is about 570 K (Ref. 14) and is quite lower than the relevant excitation energy region. If we assume a separate mechanism for energy-dependent decay process with a decay time of τ_{decay} and all other energy-independent processes with a constant decay time of τ_1, the observed relaxation lifetime τ can be described in accordance with the Matthiesen's rule

$$\frac{1}{\tau}=\frac{1}{\tau_{\mathrm{decay}}}+\frac{1}{\tau_1}. \tag{1}$$

In order to estimate the excited-electron energy dependence of relaxation lifetime, the energy-dependent decay τ_{decay} has been approximated by the empirical function $1/\tau_{\mathrm{decay}}=A(E_i-E_{\mathrm{VBM}}-E_c)^B$, and we have carried out a fit to the experimental data using Eq. (1) by a least-squares method. The fitting line using this empirical function is shown by solid line in Fig. 3, with $1/\tau_{\mathrm{decay}}=[0.015\,(E_i-E_{\mathrm{VBM}}-1.20)^{1.01}]$ fs^{-1} and $1/\tau_1=0.0007$ fs^{-1}. As shown in Fig. 3, this fitting line using an empirical function reproduces the experimental dependence fairly well. The indirect energy gap of $2H$-MoS_2 is about 1.2 eV, therefore, this result suggests that the decay rate of hot electron has an almost linear dependence on the excess energy above CBM. An important point to note is that the hot-electron relaxation in the layered semiconductor is in contrast to a prediction by Fermi liquid theory, in which the decay rate of the hot electron associated with the electron-electron scattering has a quadratic dependence on the electron excitation energy.

A possible explanation of a deviation from the Fermi liquid theory can be related to the two-dimensional layered character of electron gas in $2H$-MoS_2. In the previous TR-2PPE study for the highly oriented pyrolytic graphite (HOPG), a similar linear dependence of decay rate on the electron excitation energy has been reported.[15,16] Xu *et al.*[15] have concluded that this linear energy dependence can be quantitatively explained as a relaxation lifetime due to the acoustic plasmon emission. In the layered electron gas (LEG), the plasmons are acoustical excitations and can contribute to the quasiparticle lifetime even for the small electron excitation energy.[17,18] In the case of small interlayer separation, the acoustic plasmon emission becomes the dominant decay channel for quasiparticles, and the corresponding decay rate exhibits the linear dependence on the excess energy.[15] As a result, a possible origin of the present linear dependence of hot-electron decay rate on the excess energy above CBM might be explained by the LEG model, indicating that the acoustic plasmon scattering dominates the relaxation of hot electrons in the present layered semiconductor $2H$-MoS_2. In the form of a linear dependence of hot-electron decay rate on the electron excess energy ε, $1/\tau=[b_{ee}\varepsilon]$ fs^{-1} the proportional factor b_{ee} for a graphite has been reported to be 0.029 $\mathrm{eV}^{-1}\,\mathrm{fs}^{-1}$ by Xu *et al.*[15] Recently, Dobryakov *et al.*[19] have also reported the linear dependence of the relaxation rate on the electron excitation energy in the high-T_c oxide-superconductor $YBa_2Cu_3O_{7-\delta}$ with layered crystal structure from the femtosecond pump-probe measurements of the transient reflectivity. According to this report, the proportional factor b_{ee} for $YBa_2Cu_3O_{7-\delta}$ is 0.027 $\mathrm{eV}^{-1}\,\mathrm{fs}^{-1}$ and is almost the same as that of the graphite. On the other hand, Xu *et al.* have also reported a linear dependence of hot-electron decay rates in the layered semiconductor SnS_2.[20] The proportional factor b_{ee} for the present $2H$-MoS_2 is 0.015 $\mathrm{eV}^{-1}\,\mathrm{fs}^{-1}$ and is almost the same as that of SnS_2 reported by Xu *et al.* This proportional factor b_{ee} is in inverse proportion to the square of the average distance r_s between electrons in the layer. The lower carrier density in the semiconductor $2H$-MoS_2 than in graphite and $YBa_2Cu_3O_{7-\delta}$ can explain the differences in the proportional factor b_{ee}. This dependence of proportional factor b_{ee} on carrier density seems to indicate that the acoustic plasmon emission dominates the hot-electron relaxation. However, more systematic experiments that include carrier density dependence would be necessary.

Another possible interpretation of the deviation from the Fermi liquid behavior can be related to the band structure effects on the quasiparticle lifetimes. Gonzalez *et al.*[21] have proposed an alternative mechanism involving unconven-

tional screening that originates from the specific band structure of graphite, although also associated to the electron-electron interaction. They have concluded that the suppression of screening related to the specific band structure of graphite leads to deviations from conventional Fermi liquid behavior. On the other hand, Spataru *et al.*[22] have carried out an *ab initio* calculation of quasiparticle lifetime accounting for the band structure of graphite, as determined from the imaginary part of the self-energy operator within the GW approximation. They have also derived the significant deviations from the quadratic dependence expected from the Fermi liquid theory. Especially, they have found the pronounced anisotropies in the quasiparticle lifetimes with an anomaly originated from the lack of electron-electron scattering in the π^* band around M point of the Brillouin zone. Furthermore, Moos *et al.*[23] have reported that the hot-electron lifetimes in HOPG derived from TR-2PPE experiments exhibit an anomaly similar to that found in *ab initio* calculation around the electron excitation energy corresponding to the M point of the Brillouin zone. Therefore, another possible interpretation of the deviation from the Fermi liquid behavior in the present layered semiconductor $2H$-MoS_2 is the anisotropic quasiparticle lifetimes due to the band structure effects. However, a quantitative discussion of this band structure effect requires detailed theoretical calculation, but is beyond the scope of this Brief Report. It remains an interesting question whether the observed linear behavior is only specific to materials such as graphite, SnS_2, $2H$-MoS_2, and $YBa_2Cu_3O_{7-\delta}$, or it is generally true for layered compounds. The present TR-2PPE experiments were performed for a pristine $2H$-$MoS_2(0001)$ surface. Therefore, we believe that the observed experimental linear dependence of decay rate on the excess energy above CBM reflects the intrinsic hot-electron dynamics in the $2H$-MoS_2, and effects such as surface preparation or cesiation[23] can be excluded. We want to emphasize that a quadratic dependence of hot-electron decay rate on quasiparticle energy, dictated by the Fermi liquid theory and phase space considerations, appears not directly applicable to two-dimensional layered semiconducting materials.

In summary, we have performed a femtosecond time-resolved two-photon photoemission study of layered semiconductor $2H$-$MoS_2(0001)$ surface. It is found that the decay rates of hot-electrons depend linearly on the excess energy above CBM. This indicates that a quadratic dependence of hot-electron decay rate on quasiparticle energy, dictated by the Fermi liquid theory and phase space considerations, are not directly applicable to layered materials, and that the relaxation of hot electrons in the layered semiconductor system can be related to the acoustic plasmon scattering or band structure effects on the electron-electron scattering.

We thank L. Yan, S. Zorba, and C. J. Collison of the University of Rochester for help in the instrumentation. This work was supported by grants from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and the Advanced Technology Institute Foundation, Japan. N. J. W. and Y. G acknowledge the support of NSF Grant No. DMR-9982988.

*Author to whom correspondence should be addressed. E-mail: a-tanaka@srpe.phys.tohoku.ac.jp

[1] R. Haight, Surf. Sci. Rep. **21**, 275 (1995).
[2] H. Petek and S. Ogawa, Prog. Surf. Sci. **56**, 239 (1997).
[3] J. Cao, Y. Gao, R. J. D. Miller, H. E. Elsayed-Ali, and D. A. Mantell, Phys. Rev. B **56**, 1099 (1997).
[4] J. Cao, Y. Gao, H. E. Elsayed-Ali, R. J. D. Miller, and D. A. Mantell, Phys. Rev. B **58**, 10 948 (1998).
[5] T. Hertel, E. Knoesel, M. Wolf, and G. Ertl, Phys. Rev. Lett. **76**, 535 (1996).
[6] S. Ogawa and H. Petek, Surf. Sci. **357–358**, 585 (1996).
[7] M. Aeschlimann, M. Bauer, and S. Pawlik, Chem. Phys. **205**, 127 (1996).
[8] J. R. Goldman and J. A. Prybyla, Phys. Rev. Lett. **72**, 1364 (1994).
[9] C. A. Schmuttenmaer, C. C. Miller, J. W. Herman, J. Cao, D. A. Mantell, Y. Gao, and R. J. D. Miller, Chem. Phys. **205**, 91 (1996).
[10] F. J. Himpsel, Adv. Phys. **32**, 1 (1983).
[11] R. Coehoorn, C. Haas, J. Dijkstra, C. J. F. Flipse, R. A. de Groot, and A. Wold, Phys. Rev. B **35**, 6195 (1987).
[12] A. M. Goldberg, A. R. Beal, F. A. Levy, and E. A. Davis, Philos. Mag. **32**, 367 (1975).
[13] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College, Philadelphia, 1976).
[14] N. Wakabayashi, H. G. Smith, and R. M. Nicklow, Phys. Rev. B **12**, 659 (1975).
[15] S. Xu, J. Cao, C. C. Miller, D. A. Mantell, R. J. D. Miller, and Y. Gao, Phys. Rev. Lett. **76**, 483 (1996).
[16] K. Ertel, U. Kohl, J. Lehmann, M. Merschdorf, W. Pfeiffer, A. Thon, S. Voll, and G. Gerber, Appl. Phys. B: Lasers Opt. **68**, 439 (1999).
[17] P. Hawrylak, Phys. Rev. Lett. **59**, 485 (1987).
[18] P. Hawrylak, G. Eliasson, and J. J. Quinn, Phys. Rev. B **37**, 10 187 (1988).
[19] A. L. Dobryakov, S. A. Kovalenko, V. M. Farztdinov, S. P. Merkulova, N. P. Ernsting, and Y. E. Lozovik, Solid State Commun. **116**, 437 (2000).
[20] S. Xu, C. C. Miller, Y. Gao, D. A. Mantell, M. G. Mason, A. A. Muenter, B. A. Parkinson, and R. J. D. Miller, Chem. Phys. Lett. **272**, 209 (1997).
[21] J. Gonzalez, F. Guinea, and M. A. H. Vonzmediano, Phys. Rev. Lett. **77**, 3589 (1996).
[22] C. D. Spataru, M. A. Cazalilla, A. Rubio, L. X. Benedict, P. M. Echenique, and S. G. Louie, Phys. Rev. Lett. **87**, 246405 (2001).
[23] G. Moos, C. Gahl, R. Fasel, M. Wolf, and T. Hertel, Phys. Rev. Lett. **87**, 267402 (2001).