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学 位 論 文 題 目　　Coherent　surface　phonon　dynamics　at　alkali
　　　　　　　　　　metal-covered metal surfaces

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<div align="center">論文内容の要旨</div>

Since nuclear motions of adsorbates strongly couple to electron motions in metals due to electron-hole pair creation, strong nonadiabatic couplings between electrons and phonons are essential also in various processes on metal surfaces. For a deeper understanding of nonadiabatic couplings, it is vital to observe nuclear motions of adsorbates under electronic excitation directly in the time domain. However, these measurements are still very rare.

A laser pulse with duration shorter than the oscillation periods of surface phonons can create coherent surface phonons, i.e., a lattice mode with a large number of phonons in one mode with a constant phase-lattice relation. In this thesis, the excitation and decay mechanisms of coherent vibration of adsorbates were investigated for a deeper understanding of electron-phonon couplings. Since alkali-metal adsorption systems are a paradigm for chemisorption, their geometric and electronic structures have been extensively studied. Thus, they are suitable to explore nonadiabatic couplings at metal surfaces.

For photo-induced processes at metal surfaces, the relevant electronic transitions are categorized into two types: electronic transition between surface states and that in bulk metals. We clarified which electronic excitation is responsible for generating the coherent vibration of adsorbates by investigating its pump photon energy dependence and pump polarization dependence.

In general, decay of a coherent vibration of adsorbates is contributed by phase relaxation (pure dephasing) and population decay. The population decay channels are insensitive to surface temperature as long as the vibrational mode can be treated as a harmonic oscillator. Thus, total decay rates do not strongly depend on surface temperature, unless pure dephasing is effective. To clarify the decay mechanism of coherent phonons at alkali-metal covered metal surfaces, the pump power dependence of decay time was investigated as a function of transient surface temperature that increases with pump power.

Sample preparations were conducted in an ultrahigh vacuum chamber. The coverage and superstructure of alkali-metal adsorbates on contamination-free metal surfaces were determined by low energy electron diffraction, Auger electron spectroscopy, and x-ray photoelectron spectroscopy. Coherent surface phonons at alkali-metal adsorption surfaces were monitored with time-resolved second harmonic generation (TRSHG) spectroscopy. In this method, surface phonons were excited coherently by the irradiation of an ultrashort pump laser pulse and the evolution of coherent surface phonons was probed by monitoring intensity modulations in the second harmonic intensity of probe pulses as a function of pump-probe delay. Two sets of home-built non-collinear optical parametric amplifiers pumped by a Ti:sapphire regenerative amplifier supplied ultrashort pulses (25 fs) independently tunable from 2.0 to 2.5 eV, which were used as pump and probe pulses in TRSHG spectroscopy.

Three different alkali-metal covered surfaces were chosen: potassium on platinum (111), sodium on copper (111), and potassium on copper (111). Experimental results indicated that the excitation and dynamics of coherent surface phonons strongly depend on the combination of alkali-metal adatoms and metal substrate.

At K-covered Pt(111) surfaces, five coherently excited phonon modes were observed. K coverage dependence revealed that they are attributed to a K-Pt stretching vibrational mode and four Pt surface phonon modes. The frequency of the K-Pt stretching phonon mode depends on the superstructure of K: 5.0-5.3 and 4.5-4.8 THz for (2×2) and ($\sqrt{3}\times\sqrt{3}$)$R30°$ superstructures, respectively. Comparison of the frequencies of the Pt surface phonon modes (2.7-3.8 THz) with those at a clean Pt(111) surface suggests that the K-Pt stretching vibrational mode is weakly coupled to the Pt surface phonon modes.

At a full monolayer K-covered Pt(111) surface (0.38 ML, 1 ML = 1.51×10^{15} atoms/cm^2), the excitation mechanism and dynamics of the coherent surface phonons were extensively investigated. When the photon energy of a pump pulse was varied from 2.0 to 2.4 eV, the initial amplitude of the K-Pt stretching mode was enhanced by a factor of 2 at a photon energy resonant to the transition from the K-induced surface occupied state to the second lowest image potential state. Modulation signals of TRSHG traces disappeared when the polarization of the pump laser was changed from p- to s-polarization. The photon energy and polarization dependences indicate that the electronic transition between the K-induced surface occupied state and the image potential state is responsible for the generation of the coherent K-Pt stretching vibration. The decay time of the K-Pt stretching mode became shorter and its frequency redshifted as the absorbed fluence of the pump pulse increased. This fluence dependence was interpreted to be due to anharmonic coupling between the K-Pt stretching and lateral modes.

At Na-covered Cu(111) surfaces, two coherently excited phonon modes were observed. Na coverage dependence revealed that they are attributed to strong Na-Cu stretching resonances coupled with Cu surface phonon modes such as a surface Rayleigh phonon mode. The higher frequency phonon mode showed a redshift from 6.2 to 5.5 THz with increase of coverage from 0.14 to 0.44 ML (1 ML = 1.76×10^{15} atoms/cm^2). While the lower frequency phonon mode appeared at 0.44 ML with a Na (3/2×3/2) superstructure, this mode disappeared at 0.14 ML.

At a full monolayer Na-covered Cu(111) surface (0.44 ML), the excitation and dynamics of coherent surface phonons were extensively investigated. When the photon energy of the pump laser was varied from 2.0 to 2.5 eV, the initial amplitude of the Na-Cu stretching mode was not enhanced by the resonant electronic transition between surface states but increased with the absorbance of bulk Cu. This result

clearly indicates that the electronic transition in the Cu substrate is responsible for the generation of the coherent Na-Cu stretching vibrational modes rather than the electronic transition between surface states. This conclusion is in stark contrast to the case of K/Pt(111).

The decay time of the Na-Cu stretching mode with the frequency of 5.5 THz was 0.3 ps at the full monolayer coverage, which was much shorter than those of Cs-Pt (1.9 ps) and K-Pt (1.1 ps). As stated earlier, the Na-Cu stretching vibrational phonon mode is strongly coupled with bulk phonon modes and becomes a surface resonance mode. Thus, the fast decay of the Na-Cu stretching mode is caused by both effective population decay and pure dephasing associated with coupling to Cu bulk phonon modes. The decay time of the Na-Cu stretching mode became shorter and its frequency redshifted as the absorbed fluence of the pump pulse increased. This fluence dependence was interpreted to be due to anharmonic coupling between the Na-Cu stretching and other phonon modes.

For K-covered Cu(111) surfaces, an abrupt frequency jump of the coherent K-Cu stretching vibrational mode was observed: from 3.0 to 5.5 THz at 0.28-0.30 ML (1 ML = 1.76×10^{15} atoms/cm^2). With increase of K coverage, the decay time decreased dramatically from 0.9 to 0.4 ps at 0.28-0.35 ML. The abrupt changes in frequency and decay time occurred at around 0.30 ML. At 0.30 ML, the compression of a (2×2) superstructure of K is completed and the growth manner of K overlayer changes. The abrupt changes in frequency and decay time are associated with the changes in the adsorption site of K that influence strongly the deformation potential with respect to a K-Cu bond as well as the nonadiabatic coupling between electrons and phonons.

On metal surfaces, electrons and phonons are nonadiabatically coupled via electron-hole pair creation. This thesis made it clear that there are two kinds of electronic transitions that drive the coherent stretching vibration between alkali-metal adsorbate and metal substrate: the electronic transition between surface states and that in the substrate. This thesis also clarified that the pure dephasing as well as energetic relaxation to electrons or other phonons is significant for the decay process. The most effective pathway for decay depended on adsorption system, alkali-metal coverage, and pump absorbed fluence. The comparative study in this thesis indicates that the couplings between surface phonon modes significantly characterize the nonadiabatic couplings between electrons and phonons at alkali-metal covered metal surfaces.

論文の審査結果の要旨

　出願された博士論文は、アルカリ金属が吸着した金属表面におけるコヒーレント表面フォノンの励起と減衰メカニズムに関する実験的な研究成果をまとめたものである。論文は6章からなり英文で書かれてあり、第1章の序論、第2章の実験方法に続いて本論文における重要な実験結果と考察が第3章から5章に書かれており、最後の第6章において全体のまとめと将来への展望が記されている。

　一般に、注目する振動周期よりも十分短い衝撃を系に加えると振動子同士が位相をそろえて振動を始める、いわゆる、コヒーレント振動を誘起することができる。表面吸着系では、この振動周期で振動する巨視的な分極が表面に生成されるため、これを表面鋭敏な第2高調波発生の強度変化として観測することができる。本論文ではこの原理を用いた時間分解第2高調波発生分光により、アルカリ金属（Na、K）と金属表面（Pt(111)、Cu(111)）とのいくつかの組合せについて行われた実験的研究がまとめられている。

　第3章では、K/Pt(111)についての研究結果が述べられている。この系では、K-Pt伸縮振動のみならず複数の白金表面フォノンモードが同時にコヒーレントに励起されることを見出した。K原子が吸着していても白金の表面フォノンモードの周波数は清浄表面での過去の測定結果と大きく変わらないことから、K-Pt伸縮振動と表面フォノン間の結合は弱いことがわかった。K-Ptコヒーレント伸縮振動の初期振動強度を励起レーザーの波長、および、偏光・入射角の関数として測定することにより、表面に局在する電子状態間の遷移がこれらのコヒーレントフォノン生成の原因であることがわかった。この成果の一部はすでにPhys. Rev. Bに掲載されている。

　第4章では、Na/Cu(111)について述べられている。この系でもアルカリ金属の伸縮振動と表面フォノンモードが観測されたが、次のようなK/Pt(111)と大きく異なる点が明らかになった。まず、観測されたコヒーレントフォノンの減衰時間は極めて速い。これは、アルカリ金属の伸縮振動と銅表面フォノンの両者が強く共鳴的に結合していることを意味している。また、励起波長依存性により、コヒーレントフォノン生成には表面状態ではなく、基板の電子励起が大きく関与していることを見出した。

　第5章では、K/Cu(111)について述べられている。この系の特徴は、観測されたコヒーレント振動の振動数が、あるアルカリ金属の被覆率を境に大きく変化する点である。この原因として、上記の2つの吸着系の結果と比較することにより、アルカリ金属の被覆率の増加にともなう吸着サイトの変化が重要であると推測した。

　本研究では、コヒーレントフォノン初期振幅の励起波長依存性を測定するために、波長可変な25フェムト秒の励起パルスを発生する非同軸パラメトリック増幅器を自作するなど装置の上での工夫をすることにより、世界で始めてアルカリ金属吸着系におけるコヒーレントフォノンの生成メカニズムを明らかにすることに成功した。これらの点を鑑み、審査委員会全員一致で本申請論文は博士（理学）の学位論文として十分であると判断した。