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# HIGH RESOLUTION ELECTRON ENERGY LOSS STUDIES OF SURFACE VIBRATIONS

**Progress Report**

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## Abstract

New experimental investigations of surface vibrational properties of materials with high-resolution electron energy loss spectroscopy (EELS) are reported. The effort has focused on surface phonon dispersion measurements for copper (111) and ultrathin epitaxial films of nickel and cobalt grown on a copper (001) substrate. Data and analysis of several surface modes and resonances on Cu(111) is consistent with a modest (15%) softening of the intraplanar force constant between surface atoms. For epitaxial thin films of a few monolayers thickness of nickel on Cu (001), new film modes are identified experimentally and correspond to vibrational motion localized primarily in the film. Measurements for epitaxial films of cobalt on a Cu (001) substrate exhibit substantial flattening of the Rayleigh phonon dispersion, suggestive of surface stress in the films.

## A. Summary of Research

### Introduction

This section summarizes research progress made since the last progress report (June 15, 1988) to the time of this writing. The project is devoted to new experimental investigations of surface vibrational properties on clean metals and semiconductor surfaces and on surfaces with adsorbed layers, including metal films. The principal experimental method employed for the measurement of surface phonon dispersion is high-resolution electron energy loss spectroscopy (EELS).

The major effort this year has been devoted to surface phonon dispersion studies on ultrathin (1–10 monolayer) films of nickel and cobalt on a copper (001) substrate. There is great current interest in these films in terms of their epitaxial growth and magnetic properties. We have made substantial progress on the surface phonon properties of these materials as described below. A new experimental facility has also been under construction the past year and major features are now completed, as will be described below.

### Surface Phonons on Cu(111)

A complete paper on the surface vibrational properties of Cu (111) was published in September, 1988[Ref. 1]. A reprint of this paper is appended to this report. Since this topic was described in some detail in the last progress report, we refer the reader to the appended material.

### Surface Phonon Dispersion in Ultrathin Epitaxial Films of Nickel on Copper (001)

There has been recent keen interest in the properties of ultrathin epitaxial films of a few monolayers (ML) thickness. Iron and cobalt, for example, may be grown in metastable fcc layers on a copper (001) substrate. The investigation of the magnetic behavior of such films has therefore been one such area of interest. One principal area of work in our group this past year has concerned the vibrational properties of films of nickel 2–6 ML thick grown layer-by-layer on a copper (001) substrate. Our efforts have involved developing methods to assure good epitaxial growth of highly-ordered films in a clean ultrahigh vacuum environment. In the case of nickel overlayers care must be taken to avoid diffusion of nickel in copper. These problems were solved by careful design of the evaporation source and by restricting the substrate temperature during evaporation and post-evaporation substrate annealing. The integrity of the films was verified by low-energy electron diffraction, Auger electron spectroscopy and EELS.

Our first phonon measurements on this system were restricted to dispersion along the $\overline{\Gamma} - \overline{X}$ direction in the surface Brillouin zone. This work was accepted for publication in Phys. Rev. B[Ref. 2]. (A preprint has been distributed under separate cover.) These measurements were partly motivated by recent lattice dynamical calculations by Tong et al. dealing with the general vibrational properties of epitaxial films of Cu on Ni (001) and Ni on Cu (001)[Ref. 3]. These authors reported the nature of the surface phonon dispersion as a function of overlayer thickness along $\overline{\Gamma}$ to $\overline{X}$ in the surface Brillouin zone, based on a nearest-neighbor central force lattice dynamical slab model. Novel features predicted in these calculations include the existence of so-called film modes ($F_i$) which correspond to vibrational modes localized primarily in the overlayer. In our experiments, we reported the first observation of such modes, which are expected to be a general feature of phonon dispersion in ultrathin films[Ref. 2]. The film modes we observe lie in substantially the same frequency region above the copper bulk phonon band edge in agreement with the calculations of Tong et al.

In addition to the film modes, we also reported the Rayleigh phonon mode ($S_4$) dispersion from $\overline{\Gamma}$ to $\overline{X}$ for film thicknesses of 2–6 ML. The Rayleigh mode frequency for these films is found to be substantially higher than the clean copper $S_4$ mode but lower than the case for clean nickel. In order to better understand the nature of the lattice dynamics of the ultrathin films (which likely involve surface stress) it was found important to obtain data on the Rayleigh phonon from another symmetry direction ($\overline{\Gamma}$ to $\overline{M}$) as well. Such data was recently obtained and is being modeled theoretically by Tong and co-workers. We believe this analysis will provide a stringent test of models for surface modes in these epitaxial films. We expect to submit a complete paper on these new results by September, 1989[Ref. 4].

## Surface Phonon Dispersion in Ultrathin Epitaxial Films of Cobalt on Copper (001)

Our work on cobalt thin films parallels our work on nickel films and will be discussed very briefly here. We have measured the dispersion of the Rayleigh phonon mode from $\overline{\Gamma}$ to $\overline{X}$ for various film thicknesses (1–6 ML). This is to our knowledge the first experimental determination of the Rayleigh mode dispersion on either thin films or single crystals of cobalt. These results have been accepted for publication in Surface Science Letters[Ref. 5]. At the zone boundary we find the frequency of the Rayleigh phonon (118 $cm^{-1}$) to be higher than that of clean copper (001) (108 $cm^{-1}$) but lower than that of a nickel film (125 $cm^{-1}$) on the same substrate. Most striking, however, is the very flat dispersion of the mode. Our preliminary analysis of this result suggests that a substantial amount of stress exists within the cobalt films. In order to determine the lattice dynamics more accurately we plan additional measurements from $\overline{\Gamma}$ to $\overline{M}$ in the near future, in conjunction with a theoretical analysis by Tong et al.

## Oxygen Overlayers on Ultrathin Epitaxial Nickel Films

We have studied the Rayleigh phonon dispersion for ultrathin nickel films on a Cu (001) substrate which have been exposed to oxygen. The oxygen atoms form well-ordered $c(2 \times 2)$ overlayers on the nickel films. When exposed to oxygen the Rayleigh phonon frequency at the zone boundary ($\overline{X}$) drops 20–35 $cm^{-1}$, depending on the nickel film thickness. For example, for a 5 ML Ni film the Rayleigh phonon frequency at $\overline{X}$ is 125 $cm^{-1}$ but drops to $\sim$ 90 $cm^{-1}$ with oxygen adsorption. We also find that the Rayleigh phonon frequency in the presence of oxygen varies systematically with nickel film thickness. These results imply changes in the electronic structure of the films with oxygen exposure. We plan to publish these data in the near future when a theoretical analysis of the lattice dynamics has been completed.

### Instrumentation Development

Construction of a new experimental facility for surface phonon measurements commenced in 1988 with funding support of $90K from Indiana University. This facility consists of an ion-pumped ultrahigh vacuum system with a rotatable electron energy loss spectrometer and a sample manipulator providing both polar and azimuthal sample rotation. The system is also equipped for low-energy electron diffraction and Auger spectroscopy. Although completion of the system was planned by the fall of 1988, delays from equipment vendors resulted in substantial completion of the system this spring. Presently, the EELS control electronics is being tested and trial experiments are planned for August, 1989. This system will be applied to studies of semiconductor surfaces as outlined in the continuation proposal for this grant.

## B. Personnel

Graduate research assistants Jae-Sung Kim and Gregory Clark were partially supported during the present grant period from November 1, 1988 to December 31, 1988 and fully supported from January 1, 1989 to May 31, 1989. Mr. Kim will remain full time on the project until completion of his thesis research. Postdoctoral fellow Dr. Mohamed H. Mohamed was fully supported until assuming a position with Arizona State University in January, 1989. Candidates are being interviewed for the postdoctoral position, which is expected to be filled by September 1, 1989. The principal investigator devotes approximately 25% of his time to the project. This level of effort is expected to continue during the present grant period.

## C. Bibliography

*1. B.M. Hall, D.L. Mills, M.H. Mohamed and L.L. Kesmodel, Phys. Rev. B **38**, 5856 (1988).

*2. M.H. Mohamed, J.S. Kim and L.L. Kesmodel, Phys. Rev. B, July, 1989 (in press).

3. S.Y. Tong, Y. Chen, J.M. Yao and Z.Q. Wu, Phys. Rev. B **39**, 5611 (1989); Y. Chen, Z.Q. Wu, J.M. Yao and S.Y. Tong, ibid. **39**, 5617 (1989).

*4. Y. Chen, S.Y. Tong, J.S. Kim, M.H. Mohamed and L.L. Kesmodel (to be published).

*5. M.H. Mohamed, J.S. Kim and L.L. Kesmodel, Surface Sci. Lett. (1989). in press.

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