Study of the Solid Surfaces by Optical Second Harmonic Spectroscopy

Hideki Tanaka

School of Materials Science,
Japan Advanced Institute of Science and Technology

(Supervised by Goro Mizutani)

Keywords: SHG, surface, second-order nonlinear susceptibility, Au, GaAs

Introduction

Optical second-harmonic generation (SHG) is a powerful tool for investigating surfaces and interfaces. Its intensity is enhanced when one or two photon resonance takes place. Thus surface or interface electronic states can be found by SHG observation. However, there are few experimental studies concerning SH intensity spectrum of metal surfaces or interfaces[1]. The purpose of this study is to develop the SHG measurement system with a good performance using a tunable light source, and to establish the method for characterizing metal surfaces by SHG.

SHG measurement system

Fig. 1 shows the surface SHG measurement system constructed in this study. The excitation photon energy range of this system is from 1.0 to 2.5eV. This range is the widest among those that have ever appeared in the literature. The S/N ratio of this system is very high as 1000:1. This S/N ratio was achieved by detecting only the output SH light pulse that is synchronized with the excitation laser pulse, and using photomultiplier (PMT) having a very low dark count, and measuring the peak height of output current from the PMT. The system sensitivity was calibrated in the entire wavelength range by measuring the reflected SH intensity from an α-SiO_2 plate.

Results

In this study, I have achieved four experimental findings.

1. A new resonance of the surface SHG from GaAs(001) was found at $\hbar\omega$=1.45eV.
2. The ratio of the second-order nonlinear susceptibility elements $\chi^{(2)}_{xzx}$ and $\chi^{(2)}_{zxx}$ of the glass-Ag and glass-Au interfaces has been determined experimentally for the first time.

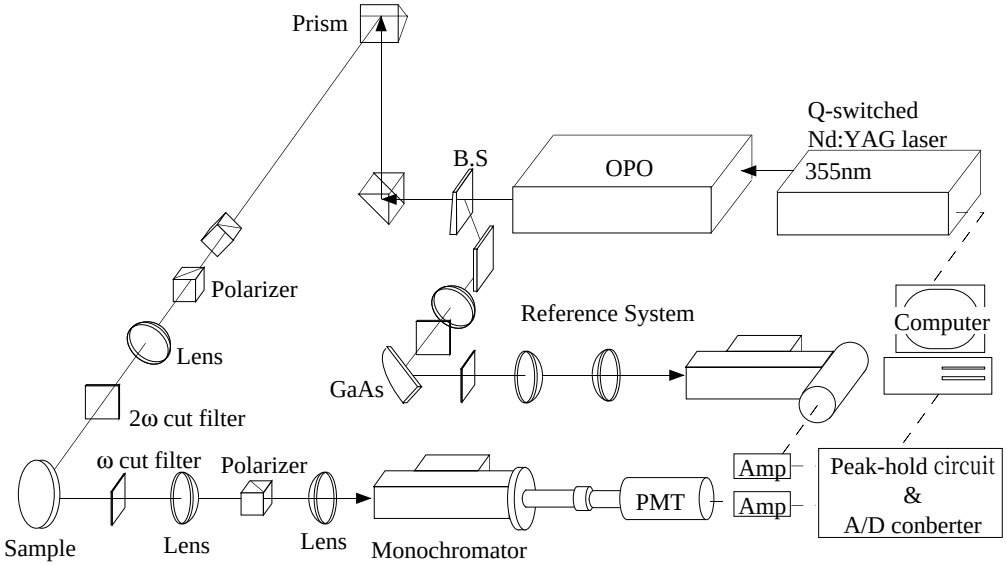

Figure 1. SHG measurement system.

3. An excitation energy dependence of the second order nonlinear susceptibility was obtained on a glass-Au interface. A peak at $2\hbar\omega$=2.5eV was discovered.

4. The SH intensity spectrum from the Au film on NaCl(100) was measured in UHV. The resonance energy of SHG of the film of thickness 60Å was $2\hbar\omega$=2.5eV and that of the film of thickness 27Å was higher than this.

1 A New Resonance of the Surface SHG from GaAs(001)

Fig. 2 shows the SH intensity from GaAs(001) in air as a function of the incident photon energy. A resonance enhancement peak at $\hbar\omega$=1.45eV has been found in the p-polarized input and p-polarized output (p-in/p-out) configuration. Because the sum frequency generation (SFG) shows a one-photon resonance at the same photon energy, the observed structure in the SH intensity curve is also due to a one-photon resonance. The bulk SH response of GaAs was separately observed in the p-in/s-out polarization configuration and does not show a resonance at $\hbar\omega$=1.45eV. Thus it was concluded that the observed resonance at $\hbar\omega$=1.45eV originates from the oxidized surface of GaAs(001). A possible candidate origin of this peak is a resonance with the inter-surface state transition. These surface states emerge due to the surface bond strain.

In this experiment also the performance of my SH measurement system was demonstrated.

2 Second-Order Nonlinear Optical Susceptibility of the Glass-Metal Interface

The ratio of the second-order nonlinear susceptibility elements $\chi^{(2)}_{xzx}$ and $\chi^{(2)}_{zxx}$ of the glass-Ag and the glass-Au interfaces have been determined at the fundamental photon

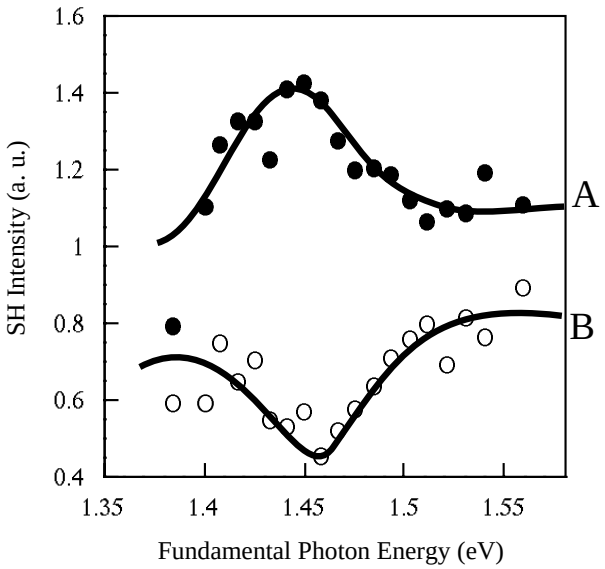

Figure 2. The SH intensity from GaAs(001) in air as a function of the excitation photon energy $\hbar\omega$. •, The SH intensity for ϕ=135^o(curve A); and ∘, the SH intensity for ϕ=45^o(curve B). ϕ is the angle between the plane of incidence and the [100] direction on the GaAs(001) face.

energy $\hbar\omega$=1.13eV. SH intensities have been measured in two polarization configurations. One is the configuration with s-polarized input and p-polarized output (s-in/p-out configuration). The other is the configuration with linearly-polarized input containing 50% of p-polarized light and 50% of s-polarized light, and with s-polarized output (s-p-*mixed*-in/s-out configuration). In s-p-*mixed*-in/s-out and s-in/p-out polarization configurations, the nonlinear susceptibility elements $\chi^{(2)}_{xzx}$ and $\chi^{(2)}_{zxx}$ contribute to the harmonic intensity, respectively. From the ratio of the SH intensities in these two configurations, I have obtained the ratio of the nonlinear susceptibility elements $\chi^{(2)}_{xzx}$:$\chi^{(2)}_{zxx}$=1.0:-0.28 for the glass-Ag interface, and $\chi^{(2)}_{xzx}$:$\chi^{(2)}_{zxx}$=1.0:-0.24 for the glass-Au interface. It has been also found that the SH intensity from the glass-Au interface deviated from the theoretically expected intensities for incident angles smaller than 20^o. It is suggested that this is either due to the higher order nonlinear optical effects of the metal bulk or due to the effect of interface steps and grain boundaries.

3 Excitation energy profile of the SH intensity from the glass-Au interface

The SHG from a glass-Au interface was observed, and the second order nonlinear susceptibility as a function of the photon energy was obtained. The sample was a Au film of thickness 100nm on a glass (BK7) substrate prepared by evaporation. Fig. 3 shows the nonlinear susceptibility as a function of the excitation photon energy $\hbar\omega$. In calculating the SH intensity, it was assumed that the zzz element dominantly contributes to the SH intensity.

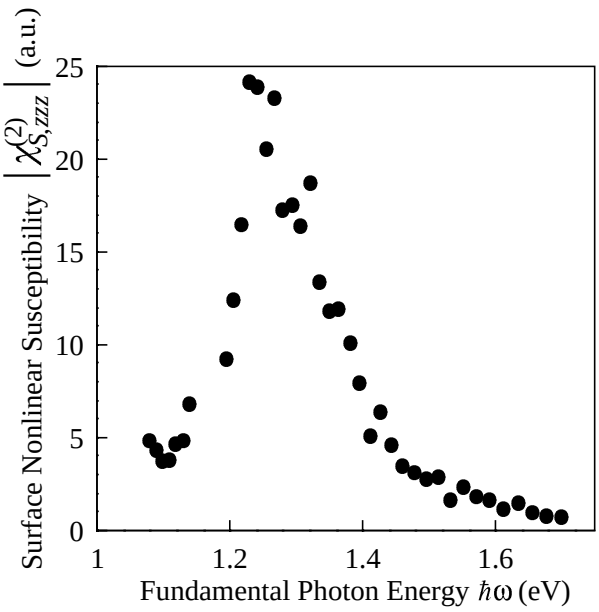

Figure 3. The SH intensity from the glass-Au interface as a function of the excitation photon energy $\hbar\omega$.

A peak is seen near $2\hbar\omega$=2.5eV. Three candidate origins of this resonance are considered:

1. The enhancement in the electric field strength by the excitation of surface plasmon polaritons,
2. The resonance with the local effective plasma frequency of free electrons at the interface, and
3. The resonance with the interband transition in which the d-electron of the interface or bulk is involved.

Each of these possibilities was checked.

1. At the rough surface, the incoming and outgoing optical light fields is enhanced because of the local-field enhancement resulting from the local-plasmon excitation. Boyd et al measured the SH intensity from several kinds of metal films on smooth and rough glass substrates. They showed that the SH intensity from the Au film is stronger than that of the Ag film on a smooth glass plate, and that the enhanced SH intensity from Ag film is much stronger than that of the Au film on a rough glass plate. Comparing my results with those by Boyd et al, I can conclude that the interface prepared in this study corresponds to the metal surface on a smooth glass plate prepared by Boyd et al. Thus we consider that there is no effect of local-field enhancement.
2. At the metal surface in a vacuum the electron density is low. The average plasma frequency in this region is the local effective plasma frequency. At the gold surface in a

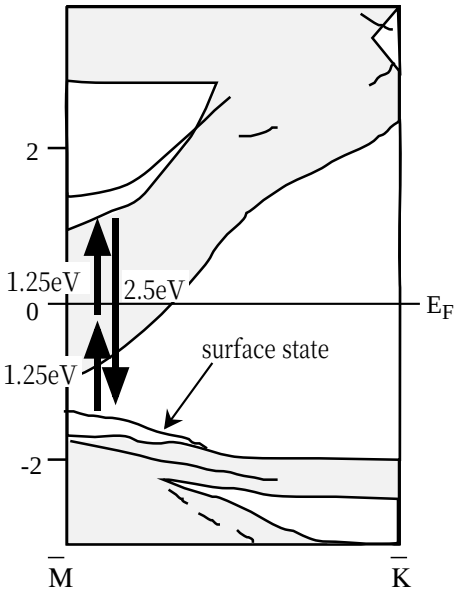

Figure 4. The SH calculated band structure of the Au(111) surface.

vacuum the local effective plasma frequency[2] is 2.4eV by calculation. The observed resonance in this study was located at $2\hbar\omega$=2.5eV in the experiment and it is close to this local effective plasma frequency. However, I can exclude this candicate for the following two reasons. Firstly, the absolute value of the nonlinear susceptibility calculated by Liebsch and Schaich[3] does not have a sharp structure like that in Fig.3. Second, the local effective plasma frequency on the glass-metal interface must be different from that of the metal surface in a vacuum. Hence Origin (2) is also excluded.

3. Fig. 4 shows the calculated band structure of the Au (111) surface[5]. We see a surface band gap of energy approximately equal to 2.5eV near the $\bar{M}$ point in the Brillouin zone. If we assume that the band gap energy of a glass-Au interface is similar to that of the vacuum-Au interface in Fig. 4, the surface interband transition is a possible candidate origin of the SHG enhancement in Fig. 3.

4 Excitation energy profile of the SH intensity from the Au film on NaCl(100) in UHV

The excitation energy dependence of the peak photon energy of the SH intensity from the Au film of thickness from 2.4Å to 60Å on NaCl(100) in UHV has been measured. The peak photon energy of the SH enhancement depended on the film thickness. The crystallinity and the surface topography of Au films were investigated by RHEED and AFM observation. The film of thickness 27Å had a single crystal face (100). The film of thickness 60Å was a polycrystal with a crystal face (111).

The resonance energy of SHG of the film of thickness 60Å was the same as that of the glass-gold interface. On the other hand, the SH resonance energy of the film of thickness

27Å was higher than that of the film of thickness 60Å. This finding indicates that these films have different surface states. I suggest that the difference of the resonance energies of the two films reflects the difference of the lattice effect on the surface states.

References

[1] L. E. Urbach, K. L. Percival, J. M. Hicks, E. W. Plummer, and H. -L. Dai, Phys. Rev. **B45**, 3769 (1992).

[2] J. E. Sipe, V. C. Y. So, M. Fukui and G. I. Stegeman, Phys. Rev. **B21**, 4389 (1980).

[3] A. Liebsch and W. L. Schaich, Phys. Rev. **B40**, 5401 (1989).

[4] N. Takeuchi, C. T. Chan, and K. M. Ho, Phys. Rev. **B45**, 3769 (1992).

Publication list

[1] H. Tanaka, H. Kurokawa, E. Kobayashi, H. Sano, G. Mizutani and S. Ushioda, Progress in Cryst. Growth & Char. of Mater. **33**, 129 (1996).

[2] H. Tanaka, T. Miyazaki, G. Mizutani and S. Ushioda, CLEO/Pacific Rim '97 TECHNICAL DIGEST 181 (1997).

[3] H. Tanaka, G. Mizutani and S. Ushioda, Surf Sci, in press.

[4] H. Tanaka, G. Mizutani and S. Ushioda, Surf Sci, submitted.

[5] H. Tanaka, T. Miyazaki, G. Mizutani and S. Ushioda, to be published.

Note: the thesis is written in Japanese.

February 20, 1998