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Raman Spectroscopy of Anodic Oxide Films on HgTe

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ABSTRACT

Laser Raman spectroscopic measurements of the anodic oxide film formed on HgTe in aqueous solutions reveal the characteristic Raman bands that appear at 422 and 684 cm^{-1}. These bands, which are different from those of crystalline $HgTeO_3$ and TeO_2 powders, may be attributed to a complex oxide of $HgTe_2O_5$ or an amorphous oxide of TeO_2 that might be formed in anodic oxidation. The heating effect on the anodic oxide film due to a focused laser beam is also discussed.

Surface passivation of compound semiconductors $Cd_x Hg_{1-x}Te$ (CMT) is of considerable importance in their utilization as photoconductive devices. One of the most common methods for surface passivation is anodic oxidation (1). In previous papers, the electrochemical reaction and the anodic oxide films of CMT and HgTe have been investigated by using x-ray photoelectron spectroscopy (XPS) and rotating ring-disk electrode (2-4). Furthermore, there have been a few papers dealing with composition of the anodic oxide (5-7). In recent years, laser Raman scattering spectroscopy has proved useful in studying the structure and composition of surface oxide films on metals. The Raman scattering spectra of bulk powder of $HgTeO_3$, $CdTeO_3$, and TeO_2 have been measured by Rhiger and Kvaas (8). In this work, a laser Raman backscattering technique is applied to the measurement of the anodic oxide films on HgTe.

Raman scattering measurements were made with a JASCO 800-T triple monochromator, and an Ar ion laser beam of 514.5 nm wavelength was used for excitation. All measurements were made in the backscattering geometry with an incidence angle of 70°. In order to minimize the effect of sample heating, a slightly defocused laser beam with an incidence power level of 25 mW was used for spectrum measurements. An attempt was, however, made to examine the heating effect on the spectra upon exposure of a focused beam with an incident power level of 50 mW.

The material studied was single crystal of HgTe with the surface of (100) plane. After electrochemical reduction of the mechanically polished surface, the material was anodically oxidized at a given electrode potential. The anodization was carried out in solution of sodium acetate-acetic acid, sodium borate-boric acid, and 0.1*M* KOH in 90% ethylene glycol-10% water. The procedure for cathodic reduction and anodic oxidation has been described in detail in a previous paper (2).

Figures 1 and 2 show the Raman scattering spectra of HgTe surfaces reduced at −0.6V *vs.* SHE (spectrum a) and oxidized at 3.0V (spectrum b) in a sodium acetate-acetic aqueous solution of *p*H 4.9. The thickness of the oxide film formed at 3.0V was found to be about 200 nm from electrochemical coulometric measurements. Spectrum a shows no characteristic bands, revealing that the reduced surface is free from any oxides and that HgTe is a weak scatterer for Raman effects. From spectrum b in Fig. 1 and 2, the Raman bands of the oxidized surface are found at the position of 422 and 684 cm^{-1}. These positions of the bands are not identical to those for TeO_2 shown in spectrum c. Furthermore, the characteristic band at 326 cm^{-1} for HgO is not observed in spectrum b for the anodic oxide. The Raman bands at 422 and 684 cm^{-1} cannot be used to clearly identify the composition of the anodic oxide. It is, however, likely that the anodic oxide, which has previously been represented by TeO_2-0.5HgO (2), is not a mixture of TeO_2 and HgO, but is a complex oxide such as $HgTe_2O_5$. Such a complex oxide has been suggested from the results by XPS and ring-disk electrode measurements (2). One may also explain the Raman bands at 422 and 684 cm^{-1} to correspond to those of amorphous TeO_2, because the amorphous oxide may exhibit the Raman band different from that of the crystallized oxide.

The spectrum with the same Raman bands as those of spectrum b in Fig 1 and 2 was obtained for the anodic oxide films with the composition of TeO_2-0.7HgO formed in the sodium borate-boric acid aqueous solution of pH 8.4 and also for the film with the composition of TeO_2-1.0HgO formed in the basic ethylene glycol solution. It appears, therefore, that the Raman scattering spectrum is

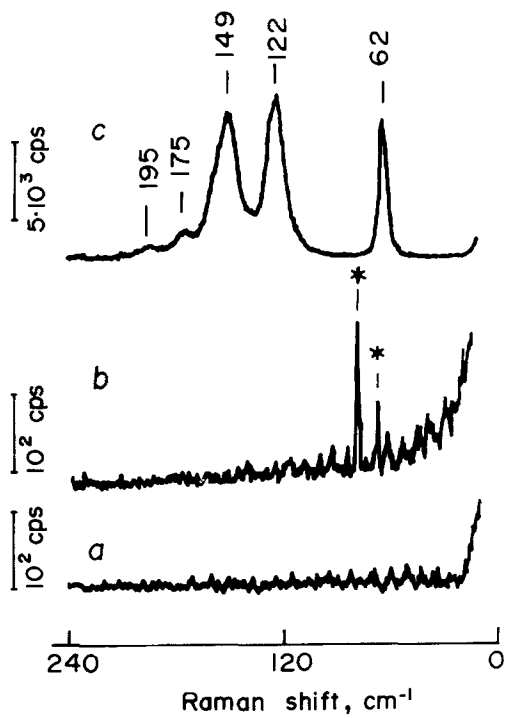

Fig. 1. Raman spectra (10-240 cm^{-1}) for HgTe surfaces reduced at −0.6V *vs.* SHE (a) and oxidized at 3.0V (b) in *p*H 4.9, and for TeO_2 powder (c). The monochromator bandpass was 1.1 cm^{-1}. The peaks marked by asterisks are emission lines of Ar ion laser.

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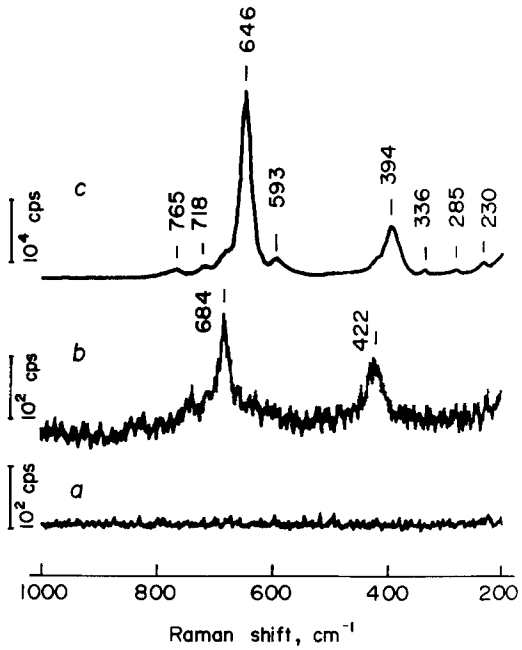

Fig. 2. Raman spectra (200-1000 cm^{-1}) for HgTe surfaces and TeO_2 powder. The monochromator bandpass was 4 cm^{-1}. Notation a, b, and c are those shown in Fig. 1.

incapable of distinguishing the composition difference in the anodic oxide films on HgTe. The characteristic positions of bands, however are markedly different from those reported for bulk powder of $HgTeO_3$:41, 59, 642, and 703 cm^{-1} (8). It is thus likely that the anodic oxide film on HgTe possesses a characteristic structure different from that of the thermally produced bulk oxide. Such a discrepancy of the Raman scattering spectrum was also observed between the oxide film on CdTe (9) and the bulk oxide $CdTeO_3$ (8).

Figure 3 shows the Raman scattering spectra of TeO_2-0.5HgO (or $HgTe_2O_5$) on HgTe measured after exposure of a focused laser beam of 50 mW. In addition to weak bands for the anodic oxide, the Raman scattering bands corresponding to TeO_2 are observed, indicating that TeO_2 is formed by the focused laser beam. This formation of TeO_2 may be represented by the following disproportionation reaction in analogy with the reaction between $HgTeO_3$ and HgTe

$$2HgTe_2O_5 + HgTe \longrightarrow 5TeO_2 + 3Hg$$

This thermal instability of $HgTe_2O_5$ and $HgTeO_3$ requires careful precaution in conducting the Raman spectroscopic studies of the oxide film on HgTe and CMT to eliminate the heating effects due to incident beam.

In summary, the characteristic Raman bands for the anodic oxide films on HgTe are found to be 68, 79, 422, and 684 cm^{-1} from determination by using a defocused laser beam with an incidence power level of 25 mW.

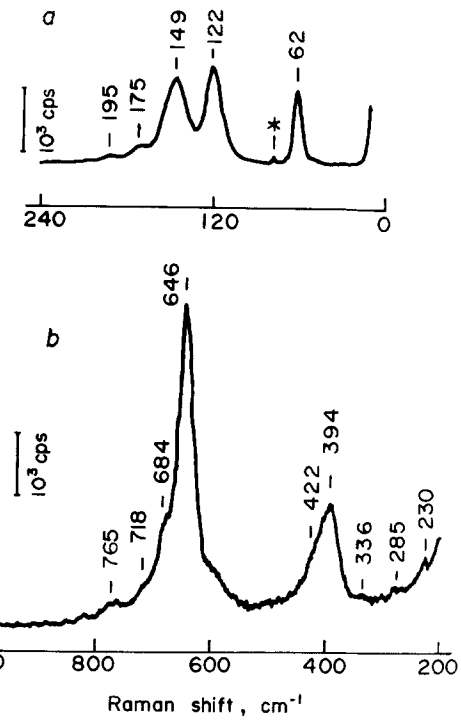

Fig. 3. Raman spectra of the anodic oxide on a HgTe surface after irradiation of a focused laser beam of 50 mW. Raman spectra were measured by using a defocused laser beam of 25 mW with the monochromator bandpass 1.1 cm^{-1} (a) and 4.0 cm^{-1} (b).

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