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LETTER TO THE EDITOR

Cathodoluminescence spectra of the oxygen-plasma-anodized film on germanium ⟨111⟩

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Abstract. The cathodoluminescence (CL) spectrum of the oxygen-plasma-anodized film on Ge ⟨111⟩ was measured in the energy region from 2.40 eV to 4.60 eV for the first time. Several photoemission bands located at 4.25 eV, 3.50 eV, 3.20 eV and 3.00 eV were obtained, and the reflection spectra were also studied, the result of which confirms these four structures. Some other discussions of the influence on CL measurements are also given.

The metal–oxide–semiconductor (MOS) structure on silicon has been widely used due to its passivation properties. Both germanium and silicon belong to the group IV elements, their structure belonging to the diamond lattice type. Thus, it was expected that good native oxide films on germanium may also have passivation properties and be of high interfacial quality. Compared with silicon, germanium has much higher electron and hole mobilities. Germanium has therefore been suggested as an attractive material for the preparation of complementary metal–oxide–semiconductor (CMOS) structures with superior performance [1]. The oxidation of a germanium surface at high oxygen pressure was reported in 1982 [2]. The native oxides formed on germanium by the wet chemical reaction method were reported in 1988 [3] and the growth of native germanium oxynitride film on germanium was reported in the same year [4]. The successful attainment of uniform native oxide films on Ge ⟨111⟩ wafers was the result of using the high-frequency oxygen-plasma-anodization (OPA) method in the film preparation [5].

Quartz glass with added germanium dioxide has been used in earlier research on the photoluminescence (PL) of GeO_2 and a characteristic PL band at 3.1 eV in oxygen deficient $SiO_2:GeO_2$ was observed long ago [6]. Later, another PL band was reported [7–9]. There were many explanations for these two structures. The latest study [10] indicated that three absorption bands at 4.95 eV (corresponding to the 4.2 eV PL) and 5.14 eV and 3.75 eV (corresponding to the 3.1 eV PL) can be attributed to the contributions of twofold coordinated Ge_2^0 centres (see figure 1).

OPA films with different thickness on an n-type germanium ⟨111⟩ wafer were used as three samples in our measurements. The resistivity of the wafer was 0.92–1.06 Ω cm. The refractive index and the thickness of the film on germanium were determined by using a TP-83 type ellipsometer with microprograms made by Beijing Information Optics Institute.

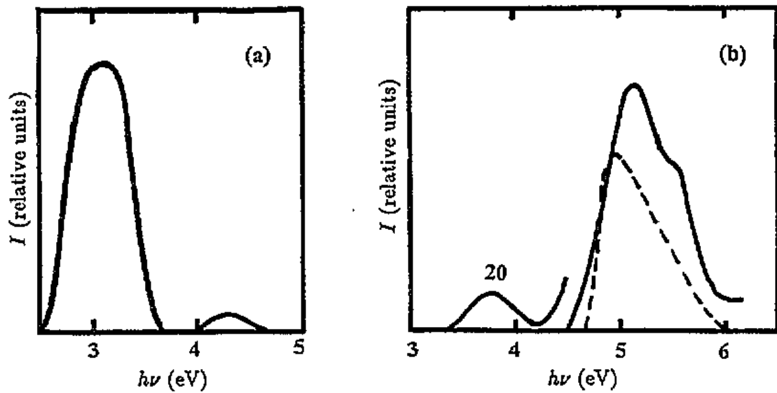

Figure 1. (Data from [10]). (a) PL spectrum of 90% $SiO_2:10\%\ GeO_2$ glass, excitation energy 4.95 eV. (b) PL excitation spectra for the 3.1 eV band (full line) and the 1.2 eV band (dashed line).

The rotating polarizers were made of Polaroid film and the indicator was of the null type. The wavelength of the He–Ne laser illumination was 632.8 nm. Two groups of ellipsometric parameters (Φ_1, ϕ_1; Φ_2, ϕ_2) were measured at incidence angles of 70° and 75° respectively. The refractive index and the thickness of the transparent thin films on germanium may be determined using the ellipsometric parameters, the complex refractive index of germanium [11], the ellipsometric equations [12] combined and a microprocessor. The refractive index n_i and the thickness T_i of the films are shown in table 1. The values of T_i are in agreement with that of vitreous GeO_2 [14] and those of n_i also agree with the results measured by the oil soak method (OSM) used in [13] and [14].

Table 1. Thickness and refractive index of the OPA film on Ge (111) (the data in brackets were measured by OSM).

Samples	T_i (nm) (i = 1, 2, 3)	n_i (i = 1, 2, 3)	Sample colour
I	40±1	1.64±0.01(1.64)	light brown
II	78±1	1.64±0.01(1.64)	dark brown
III	106±1	1.65±0.01(1.66)	blue

CL spectra were obtained at room temperature using a 0.3 m monochromator with a grating blazed at 350 nm and a XP2020Q photomultiplier. The intensity of the electron current on the target was 10^{-6} A cm^{-2} with energy 4 keV. There was a liquid nitrogen trap between the chamber and the turbo pump. The working pressure in the system was 10^{-5} Pa. A magnetic coil was used to deflect the electron beam in order to prevent direct light from the filament illuminating the target. The resolution of the monochromator was 1 nm. The CL spectra measured in the energy region from 2.40 eV to 4.60 eV are shown in figure 2. The result shows that the spectra contain five emission bands at 4.25 eV, 3.50 eV, 3.20 eV, 3.00 eV and 2.70 eV. There is some band splitting near 3.00 eV for sample I and sample III and near 4.25 eV for sample II. The photoemission intensity increases with film thickness especially in the 3.00 eV, 3.20 eV and 4.25 eV bands which indicate the presence of intrinsic structures of GeO_2 (see table 2). The reason for the disappearance of the 2.70 eV band, which is related to the increase of sample thickness (see figure 2), will be discussed later in this letter.

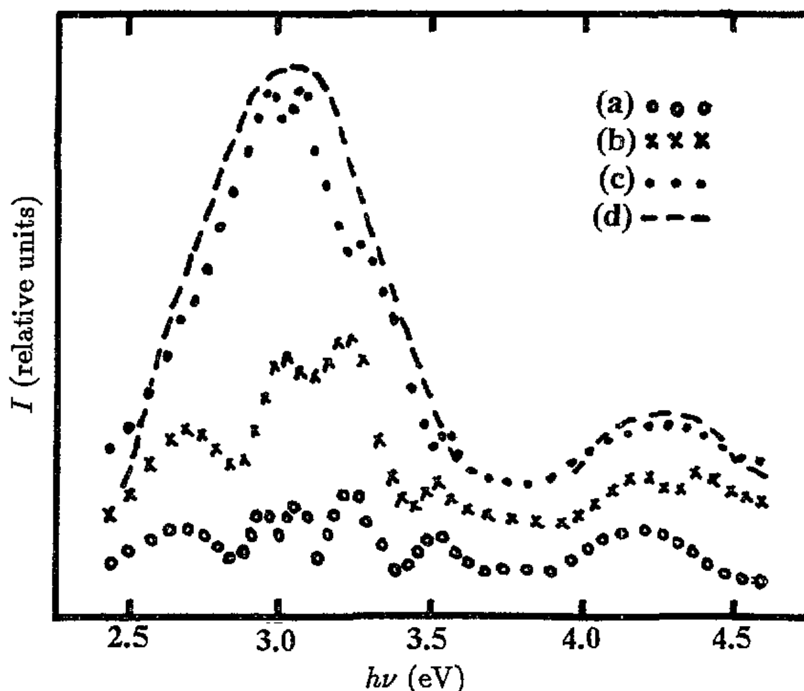

Figure 2. CL spectra of the OPL film on germanium (111). (a) Sample I, $T_1 = 40$ nm; (b) sample II, $T_2 = 78$ nm; (c) sample III, $T_3 = 106$ nm; (d) PL spectrum of 90% SiO_2 : 10% GeO_2 glass [10].

Table 2. The dependence of the CL intensity at five structures on the film thickness.

Location of photon-emission peak (eV)	2.70	3.00	3.20	3.50	4.25
CL intensity of sample III	—	10.0	6.4	2.2	3.0
CL intensity of sample II	2.4	3.5	4.0	1.8	1.7
CL intensity of sample I	1.2	1.4	1.6	1.3	1.3

In order to obtain some information about the dispersion of the OPA films, we measured the reflection spectra of samples I and II using a UV-240 Recording Spectrophotometer (Shimadzu, Japan). The wavelength range of the machine was 190–900 nm. The light sources were a 50 W halogen lamp and a deuterium lamp which had an automatic mirror changeover linked with the wavelength and automatic switching on of the lamps according to the wavelength range selected. The monochromator was an aberration-corrected Czerny–Turner mounting with a blazed holographic grating. The spectral bandwidth could be varied between 0.008 nm and 5 nm in 0.001 nm steps. The resolution was better than 0.15 nm and stray light was less than 0.05% at 340 nm. The wavelength readout was a four-digit LED display readable to 0.1 nm and the wavelength accuracy was ±0.3 nm with automatic wavelength correction. The photometric system was a double-beam, direct ratio recording type using dynode feedback. A digital recorder of thermal-graphic-printer type was controlled by computer.

The reflection spectra measured in the energy region from 2.00 eV to 6.20 eV are shown in figure 3. The curve from 2.40 eV to 4.60 eV is rather smooth indicating unclear dispersion

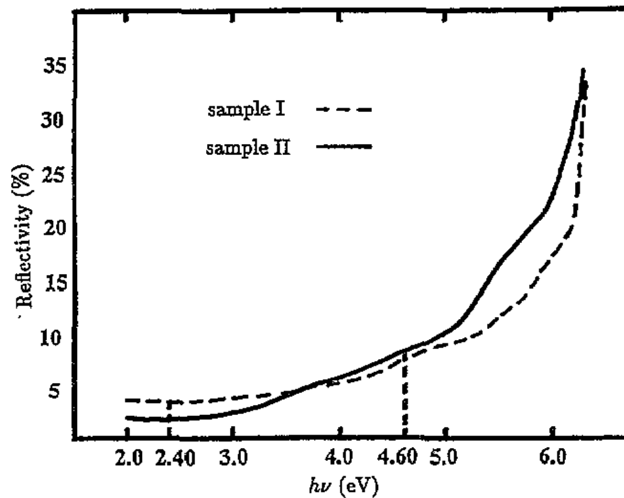

Figure 3. Reflection spectra of the OPA film on germanium ⟨111⟩.

Table 3. Photoemission intensities of the OPA film compared with that of the germanium wafer (the data are from [17]).

Photoemission energy (eV)	2.7	2.9	3.0	3.1	3.2	3.5	3.6	3.9	4.1	4.3	4.4
CL intensity of sample I (I_1)	1.2	2.2	1.4	2.2	1.6	1.3	1.0	1.0	1.2	1.3	1.2
CL intensity of Ge (I_2)	1.0	1.4	1.4	1.3	2.0	1.3	1.5	1.5	1.3	1.5	1.3
I_1/I_2	1.2	1.6	1.0	1.7	0.8	1.0	0.7	0.7	0.9	0.8	0.9

in the energy region. Thus, we know that the peak locations are correct indicating the direct transitions between bands.

Another factor influencing the CL spectra may arise from the photoemission of the germanium wafers. It is therefore necessary to calculate the sample penetration depth of the electron beam. This can be estimated from the following formulas [15, 16]:

$$R_e = (0.398/\rho)E_b^{1.75}\ (\mu\mathrm{m}) \tag{1}$$

or

$$R_e = \left(0.0276A/\rho Z^{0.089}\right)E_b^{1.67}\ (\mu\mathrm{m}) \tag{2}$$

where ρ is the density of the material (for amorphous germanium dioxide $\rho = 3.627$ g cm^{-3}), E_b is the energy (keV) of the electron beam, A is the atomic weight in g mol^{-1} and Z is the atomic number. In our experiment, E_b is equal to 4 keV, $Z = 48$ and $A = 104.59$. Thus, we obtain

$$R_{e1} = 0.124\ \mu\mathrm{m} = 124\ \mathrm{nm} \qquad \text{(from (1))}$$

or

$$R_{e2} = 0.258\ \mu\mathrm{m} = 258\ \mathrm{nm} \qquad \text{(from (2))}.$$

The thicknesses of all the samples are smaller than both R_{e1} and R_{e2}. In this case, the photoemission of the wafer is strongly absorbed by the OPA film. This is why the 2.7 eV structure diminishes with increasing sample thickness. The relative photoemission intensity of sample I compared with that of germanium ⟨111⟩ is shown in table 3.

To avoid irradiation damage on the OPA film, our sample shelf was rotated before each new set of data was collected so that the electron beam was always incident on a fresh surface of the sample. This was to prevent distortion of the spectra by damage. The dependence of CL intensity on irradiation time of sample III for the five structures is shown in figure 4. We can see that the intensity of four of the structures decreases rapidly after 5 min of irradiation indicating radiation damage of the film. An increase in the intensity of the 4.25 eV band after 6 min can be attributed to co-contributions from the film and the wafer.

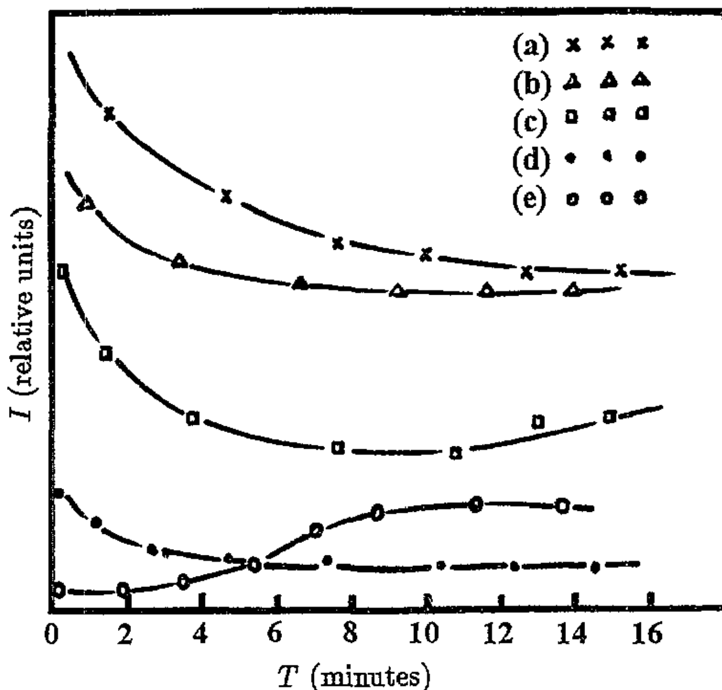

Figure 4. Dependence of cathodoluminescence intensity on the irradiation time at (a) 3.00 eV, (b) 3.20 eV, (c) 2.70 eV, (d) 3.50 eV, and (e) 4.25 eV.

In addition to the spectral features observed in earlier PL work, we have also obtained data for three other direct transitions between bands. It is interesting to note that the 3.1 eV PL band in figure 1 has a certain resemblance to an envelope function of the three CL structures at 3.00 eV (perhaps 2.95 eV and 3.05 eV splitting, see figure 3), 3.20 eV and 3.50 eV. Further work on the photoemission mechanism is required in order to obtain a detailed band structure of GeO_2, the results of which would certainly be very useful for both the understanding and application of germanium CMOS.

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