

Degradation of Cleaved LnSb (Ln = La, Ce) by Reaction in Ultrahigh Vacuum and Air

Masaoki Oku

Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aobaku, Sendai 980, Japan

Takashi Suzuki

Department of Physics, Faculty of Science, Tohoku University, Aramaki Aza Aoba, Sendai, Aobaku 980, Japan

The degradation of LaSb and CeSb in ultra high vacuum and air has been studied by XPS. The exposure of the surfaces cleaved *in situ* to the XPS spectrometer vacuum, produced with a cryo pump, slowly changes them into lanthanide oxides and elemental antimony. The cleavage of LaSb in air also induced oxidation of the elemental antimony. The binding energies of $\text{Sb}_{3/2,5/2}$ of elemental antimony produced in the vacuum were the same as those of bulk metal Sb. However, a chemical shift of the level of the elemental Sb in decomposition layers on the samples cleaved in air was positive for LaSb and negative for CeSb.

INTRODUCTION

The correct theoretical description of the electronic structure of the Ce system is still highly controversial. In this sense, Ce mono-pnictides belong to one of the most attractive systems because they have very simple electronic structures with compensated semi-metals, as revealed by the observation of the de Haas–van Alphen effect, and show particularly interesting physical properties.¹ Recently, several satellite peaks were found in Ce 3d XPS and 4f PES, Sb 4d XPS and La 3d XPS in cerium and lanthanum antimonides.^{2,3} The spectra were explained by the screening effects of both the 4f and the 5d electrons.⁴

Photoelectron (PE) \Rightarrow Bremsstrahlung spectroscopic (BIS) studies of lanthanide compounds require a careful analysis of the spectra with signals from the bulk or from the surface. If this is omitted, wrong conclusions are drawn concerning the bulk electronic structure of lanthanide compounds. It is particularly important to specify fine structure and weak signals such as satellite peaks in electron spectroscopies. This is the main motivation in this work, which carefully examined the surface and degradation effect on the profile of the x-ray photoelectron spectra in LaSb and CeSb.

The interaction between intermetallic compounds of rare earth and transition metals and oxygen has been an interesting subject in the preparation of catalysts^{5,6} and hydrogen storage.^{7,8} In general, exposure of the intermetallic compounds to an atmosphere of low oxygen partial pressure leads to selective oxidation of the rare earth component, with the transition metal remaining in a reduced state. However, the interaction for rare earth pnictides has not been reported.

In this report, the spectral variations of lanthanide 3d XPS of LaSb and CeSb due to exposure to the vacuum in an electron spectrometer have been studied. The degradation of the samples in air is also studied.

EXPERIMENTAL

A Surface Science Laboratories x-ray photoelectron spectrometer (SSX-100) with a monochromatic Al K α source having a 300 μm by 450 μm x-ray spot size was used. The vacuum of the spectrometer was 1.3×10^{-7} Pa or better.

The preparation method of the single crystals has been described previously.² The single crystals were bonded with vacuum-compatible conductive resin (Tokyo Ink, Rexbond T 100) between two copper pipes. If the sample treatment was not noted, the single crystals were cleaved in a preparation chamber with a gas pressure equivalent to the main chamber and then they were moved to the main chamber. It took ~ 2 min to start XPS measurement after the sample cleavage. The angle between the cleaved surface (100) and the detected electron beam was set to 35°.

RESULTS AND DISCUSSION

Chemical reaction between cleaved surface of LaSb and the residual gases in the spectrometer

When a single crystal of LaSb was exposed to the ultrahigh vacuum of the spectrometer after cleavage of the sample, the La 3d_{3/2,5/2} and Sb 3d_{3/2,5/2} x-ray photoelectron spectra change as shown in Fig. 1. It took 2.9 and 1.4 min to measure the La and Sb regions, respectively. The peak heights of La and Sb peaks were normalized to the height of La 3d_{5/2} of spectrum (a) recorded immediately after the cleavage. The spectrum of the scan that was started 10 min after the cleavage agreed with spectrum (a). Any adsorbed species on the surface decrease the intensities of La or Sb levels, which

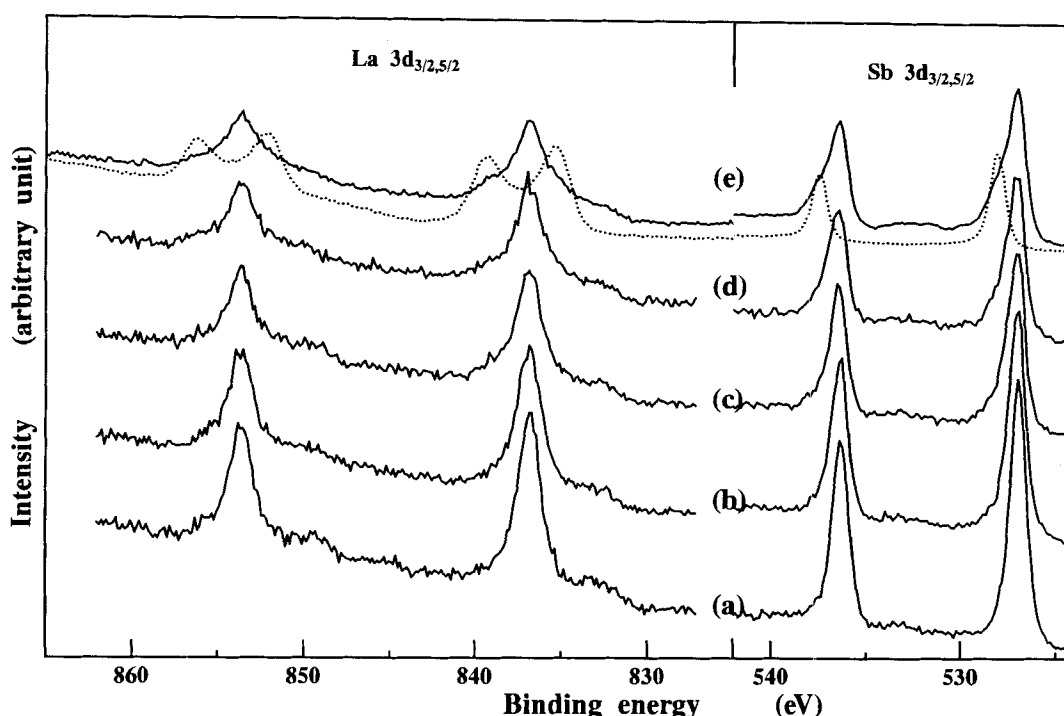


Figure 1. Time dependence of La and Sb 3d x-ray photoelectron spectra of LaSb cleaved in the spectrometer. It took 2.9 m for La 3d and 1.4 min for Sb 3d regions to obtain the spectra. The following times are those between cleavage and scan start: (a) 2 min, (b) 37 min, (c) 75 min, (d) 118 min, (e) 174 min. The dotted line in the La 3d region represents the La 3d spectrum for the oxide on LaSb cleaved at air and lightly sputtered by Ar ions. The dotted line in the Sb 3d region is the Sb 3d spectrum for metal Sb.

indicates that the amounts of adsorption of the cleaved surface are negligibly small within 15 min after cleavage.

Furthermore, the La 3d spectral profile at (a) is in agreement with the spectrum taken from the surface scraped in 1×10^{-8} Pa.² Then, in any following discussions, it can be postulated that spectrum (a) originates from the intrinsic property of LaSb. The dotted line in the region of La 3d in Fig. 1 is a spectrum of La 3d_{3/2,5/2} for the sample lightly sputtered in the spectrometer after cleavage of LaSb in air. The dotted line

in the Sb 3d region represents Sb 3d_{3/2,5/2} of Sb metal sputtered by argon ion.

The intensity ratio of the final states of f^0 to f^1 of La 3d_{5/2} for the intermetallic compounds of lanthanum is generally larger than that for metal lanthanum.⁹ The intensity ratio of f^1 (at 837 eV) to f^0 (at 833 eV) for spectrum (a) was nearly equal to that reported for the metal. The spectral profile of Sb 3d was the same as that of antimony metal, where the peak was 60% Gaussian + 40% Lorentzian. The chemical shift from

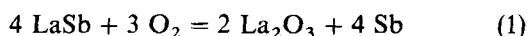
Table 1. Binding energy (E) and chemical shift (eV)^a of Sb 3d_{3/2} and 3d_{5/2} for various states

	3d _{3/2}	3d _{5/2}	ΔE
LaSb cleaved in vacuum	536.3	526.9	-1.2
Sb in degraded layer of LaSb in vacuum	537.3	528.0	0
Sb in degraded layer of LaSb in air	537.8	528.0	0.5
Sb oxide in degraded layer of LaSb in air	540.2		
CeSb cleaved in vacuum	536.3	527.0	-1.2
Sb in degraded layer of CeSb in vacuum	537.3	528.1	0
Sb in degraded layer of CeSb in air	537.0	527.6	-0.5
Bulk metal Sb	537.5	528.1	
Oxide on bulk metal Sb	540.2		
Sb ₂ O ₃	539.7 ¹⁰		
	539.6 ¹¹	530.3 ¹¹	
Sb ₂ O ₄	540.3 ¹⁰		
	540.0 ¹¹	530.5 ¹¹	
Sb ₂ O ₅	540.6 ¹⁰		
	540.6 ¹¹	531.1 ¹¹	

^a Chemical shift $\Delta E = E_b - E_b$ (bulk metal Sb).

bulk metal antimony to LaSb was -1.2 eV. The binding energies and chemical shifts of the Sb 3d level of various chemical states are summarized in Table 1. The negative chemical shift was observed in other antimony intermetallic compounds.¹²

It is clear that the peak heights of La and Sb decrease with exposure to the vacuum of the spectrometer. The apparent intensity ratio of the peaks (837/833 eV) also decreased. The most important features are the following. The maxima of the dotted line in the La 3d_{5/2} region are 835.2 and 839.3 eV, whose energy splitting equals that of lanthanum oxide. Although the higher binding energy peak was not observed in the spectrum of the first scan, it was observed after 73 min (c) and increased with time. The photoionization cross-section of O 1s is small (Scofield's theoretical values: La 3d_{5/2}, 28.1; Sb 3d_{5/2}, 16.4; O 1s, 2.92).¹³ It is therefore not strange that an O 1s peak cannot be observed between Sb 3d_{3/2} and 3d_{5/2} when the lanthanum oxide peaks are observed in the La 3d region. The other important point is that the Sb peaks of the sample exposed to a vacuum for a long time can be divided into two sets of peaks. The higher binding energies of Sb 3d_{3/2} and 3d_{5/2} (537.3 and 528.0 eV) coincide with those of bulk metal Sb. Then, the chemical reaction between the LaSb and gases in the spectrometer can be written by Eqn (1)



There are many gases containing oxygen atoms, such as O₂, H₂O and CO, in the vacuum. Although it is considered that some reactions occur in the oxidation of the sample, Eqn (1), here stands for the reactions.

Further exposure up to 30 h did not change the spectrum from spectrum (e).

Schlapbach has reported that the exposure of LaNi₅ cleaved in a vacuum to small amounts of oxygen induces oxidation of lanthanum but no oxidation of nickel.⁸ Then, its reaction is similar to Eqn (1), but the chemical shift of the Ni 2p_{3/2} level in the decomposition layer is not mentioned.

One of the authors reported that the surface segregated by antimony in iron-antimony alloy depressed the oxidation of iron.¹² Then, it is considered that lanthanum slowly oxidizes under the existence of antimony in the surface of the sample. The slow reaction makes it possible to obtain the x-ray photoelectron spectra representing the intrinsic properties of LaSb even at a relatively high pressure of 10^{-7} Pa.

The La 3d_{5/2} for LaSb reported by Baer *et al.*¹⁴ consisted of three peaks and looks like spectrum (e) in Fig. 1 of this report. Although the detailed vacuum condition to measure XPS was not described, it is supposed that the surface that was cleaved or abraded with a tungsten brush or an Al₂O₃ file was oxidized during the long time to take the spectrum.

Oxidation for cleavage of LaSb in air and Ar sputtering of the oxidized surface

The sample cleaved in air was placed in the spectrometer and air was pumped out 5 min after the cleavage. The surface gave the spectra in Fig. 2. Each of the La 3d_{3/2} and 3d_{5/2} peaks consisted of two peaks, and the binding energies of the La 3d_{5/2} peaks were 835.3 and 839.4 eV. These values and the spectral profile of the La 3d level coincided with those reported for La(OH)₃.¹⁵

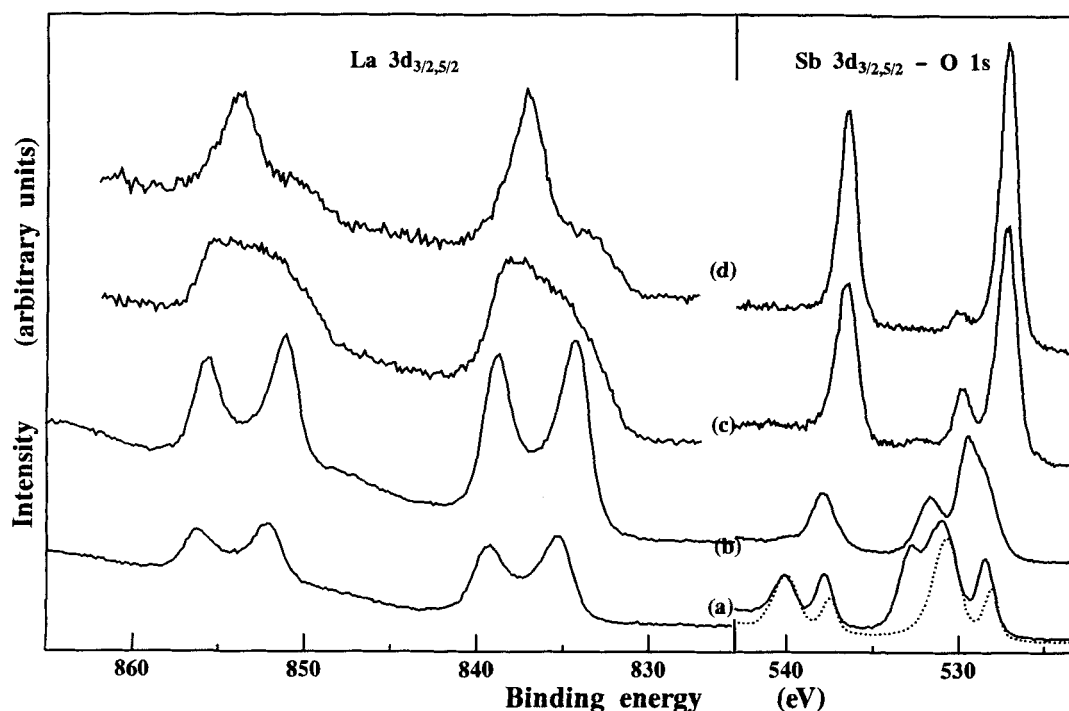


Figure 2. X-ray photoelectron spectroscopy variation of La 3d, Sb 3d and O 1s of LaSb cleaved in air with ion sputtering using argon ions at 2 kV: (a) as received; (b) emission current 0.3 mA, sputtering time 5 min; (c) as in (b) + emission current 1 mA, sputtering time 10 min; (d) as in (c) + sputtering time 20 min. The dotted line is the spectrum for Sb metal cleaved in air.

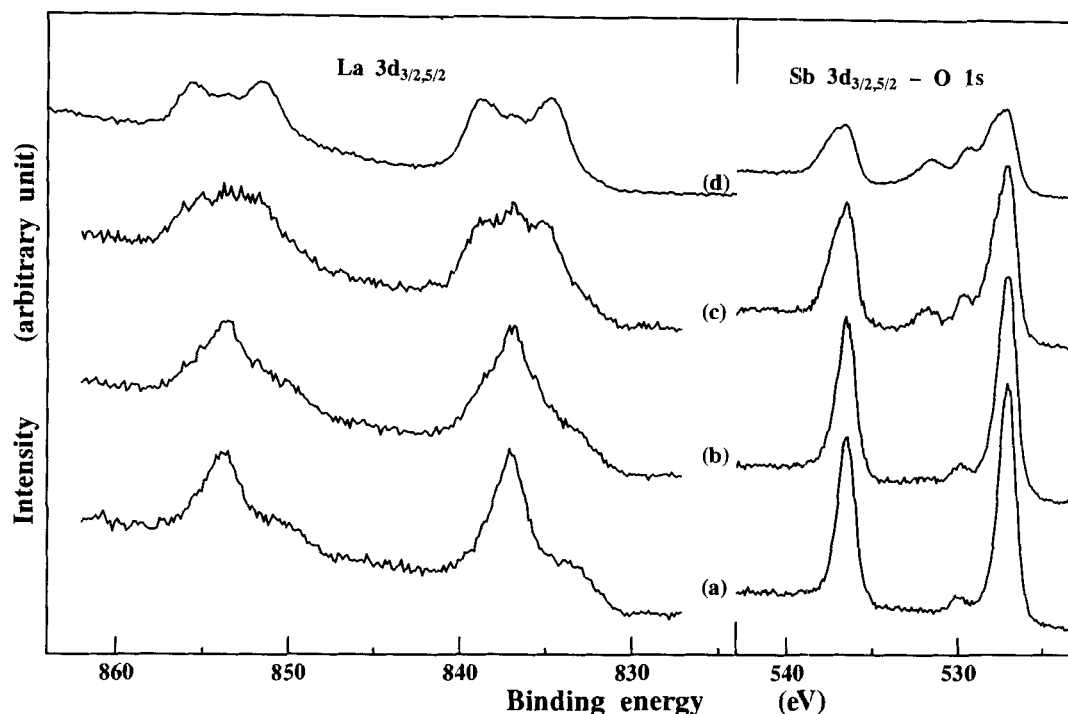


Figure 3. Time dependence of La 3d, Sb 3d and O 1s x-ray photoelectron spectra after ion sputtering of the surface of LaSb cleaved in air. (a) Same as (d) in Fig. 2. X-ray photoelectron spectroscopy measurement was started after sputtering at 11 min (b) and 40 min (c).

The light argon ion sputtering changed them to 834.2 and 838.9 eV as shown in (b), where the reported values for La_2O_3 are 834.6 and 838.6 eV.¹⁶ Thus, it is conjectured that the states of lanthanum in (a) and (b) are $\text{La}(\text{OH})_3$ -like and La_2O_3 -like, respectively.

The LaSb surface cleaved in air had two peaks for Sb $3d_{3/2}$. The overlapping of Sb $3d_{5/2}$ and O 1s gave three peaks at 528.4, 530.9 and 532.8 eV. The binding energy of 540.2 eV coincided with that of an oxide peak on Sb metal cleaved in air. This spectrum is shown by the dotted line in Fig. 2. From the chemical shifts, it is considered that the higher binding energy peak in Sb 3d is Sb_2O_3 -like.

The antimony oxide peak disappeared with light ion sputtering. Although the binding energies of 528.4 and 537.8 eV are slightly larger than that of 528.1 and 537.5 eV for metallic Sb, the peak may originate from the elemental antimony. It is well known that binding energies of peaks of metals sometimes change with the matrix. Chemical shifts from metal bulk to elemental particles on oxides are positive in almost all cases,¹⁷⁻¹⁹ and it is considered that the elemental particles of Sb are distributed in lanthanum oxide or hydroxide. It is interesting that the binding energy of the state is different from that of elemental Sb produced by the slow reaction rate of Eqn (1) in the x-ray photoelectron spectrometer.

Further addition of ion sputtering decreased the intensity of lanthanum oxide and finally gave spectrum (d). The intensity ratio La $3d_{5/2}$ /Sb $3d_{3/2}$ /Sb $3d_{5/2}$ + O 1s showed that the apparent La/Sb/O atomic ratio was 13:9:78 at (a), 20:4:76 at (b), 45:23:32 at (c) and 50:42:8 at (d), calculated with Scofield's photoionization cross-sections and an attenuation length proportional to $E_k^{0.7}$ (E_k is the kinetic energy of the electrons).

The results of Fig. 2 suggest the following reactions. When a single crystal of LaSb is cleaved in air, a reaction according to Eqn (1) occurs. The elemental antimony is immediately oxidized to the oxide, and La_2O_3 changes into the hydroxide. As the attenuation length of electrons having a kinetic energy of 1480–530 eV is ~ 1 nm, the thickness of the altered layer is larger than ~ 5 nm. The very low concentration of antimony in state (b) shows that there is a zone that is deficient in antimony.

The apparent intensity ratio of the final states of f^1 to f^0 at (d) (1/2.5) was larger than that at (a) (1/4) in Fig. 1. Although the intensity ratio increased with the formation of lanthanum oxide, the apparent La/Sb/O atomic ratio at (d) indicated that almost all of the lanthanum atoms were not oxidized. Furthermore, the full widths at half-maximum (FWHM) of Sb $3d_{3/2}$ and $3d_{5/2}$ (1.2 eV) were larger than 1.0 eV at (a) in Fig. 1, although the binding energies for both states were the same. The profiles of La and Sb 3d may be interpreted as damage caused by the ion sputtering. The ion sputtering produces the damaged layer on LaSb, and results in a different atomic ratio of La to Sb and different bonding between them from those of LaSb. The broad Sb peak and high intensity ratio of f^1 to f^0 are due to the damage layer, where the intensity ratio is sensitive to the atomic ratio of lanthanum to the counter-element in its alloys or intermetallic compounds.⁹

Chemical reactions of LaSb surface sputtered by ions and residual gases in the spectrometer

The exposure of the sample after ion sputtering gave the XPS variation shown in Fig. 3. The intensity of lantha-

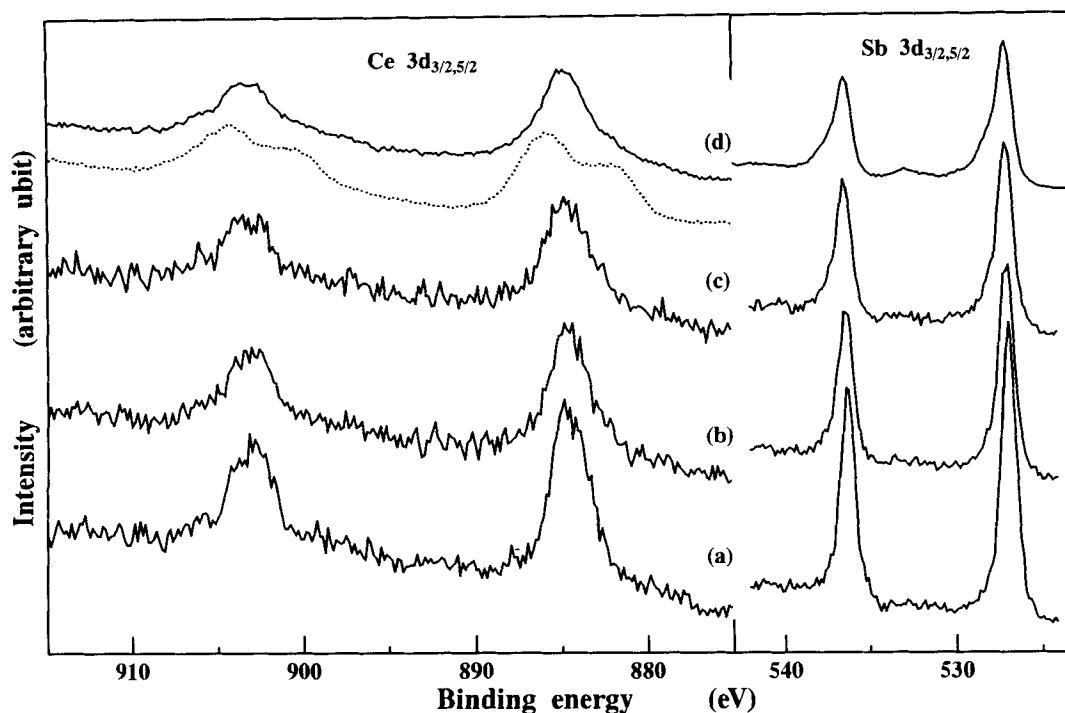


Figure 4. Time dependence of Ce and Sb 3d XPS spectra of LaSb cleaved in the spectrometer. It took 2.9 min to obtain the spectra for the Ce 3d region and 1.4 min for the Sb 3d region. The following times are those between cleavage and scan start: (a) 2 min, (b) 75 min, (c) 170 min, (d) 350 min. The dotted line in the Ce 3d region represents the Ce 3d spectrum for the oxide on cleaved CeSb in air.

num oxide increased with time and elemental antimony was observed. The intensity ratio of elemental to inter-metallic compound (539.5/553.6 eV in Sb 3d_{3/2}) of spectrum (c) in Fig. 3 was larger than that of spectrum (e) in

Fig. 1, i.e. although the time of exposure to the vacuum in Fig. 3 was shorter than that in Fig. 1, the rate of chemical reaction of Eqn (1) for the ion-sputtered surface was larger than that for the surface cleaved in a

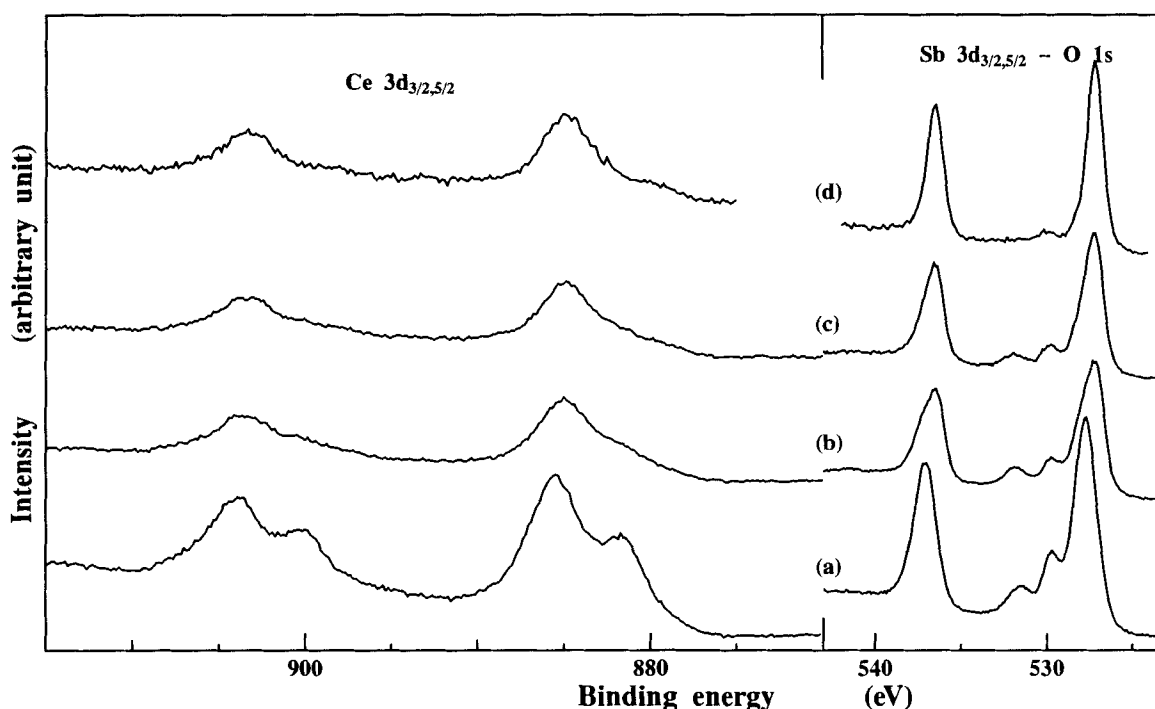


Figure 5. X-ray photoelectron spectroscopy variation of Ce 3d, Sb 3d and O 1s of CeSb cleaved in air with ion sputtering using argon ions at 2 kV: (a) as received; (b) emission current 0.3 mA, sputtering time 2 min; (c) 12 min; (d) 35 min.

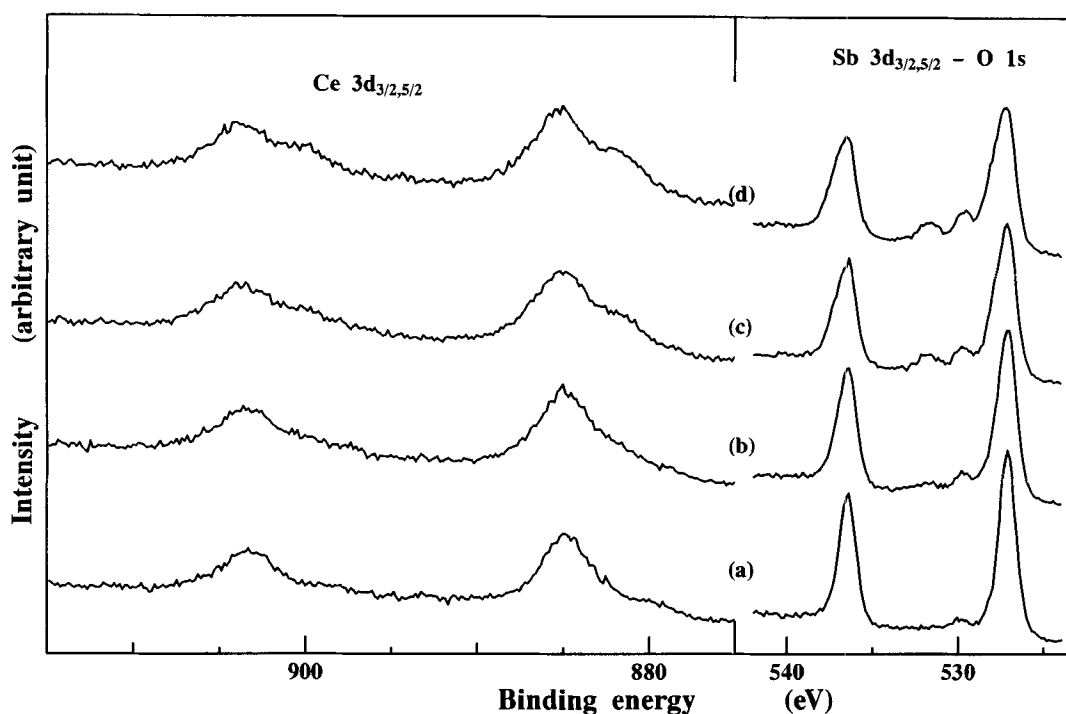


Figure 6. Time dependence of Ce 3d, Sb 3d and O 1s x-ray photoelectron spectra after ion sputtering the surface of CeSb cleaved in air. (a) Same as (d) in Fig. 5. X-ray photoelectron spectroscopy measurement was started after sputtering for 9 min (b) and 35 min (c).

vacuum. The high rate in Fig. 3 may be caused by reactive non-stoichiometric intermetallic compound in the damaged layer, as described before.

Chemical reactions of CeSb in the spectrometer and air

Figure 4 shows the XPS variation of Ce and Sb 3d spectra after cleavage in a vacuum. The Ce 3d spectrum of the fresh surface has a profile that is similar to that of α -Ce metal.¹⁹ The binding energy of Sb 3d was the same as that of LaSb. Although the hybridization between lanthanide 4f and Sb 5p levels in CeSb is different from that in LaSb,²⁰ the difference does not affect the Sb 3d binding energy. The exposure of the sample to the vacuum gave cerium oxide and elemental antimony, as shown at (d). The chemical reaction is written by Eqn (2)



When a single crystal of CeSb is cleaved in air, cerium oxide and elemental antimony peaks are observed, as shown in Fig. 5. The Ce 3d_{5/2} peak consisted of two peaks with an energy separation of 5 eV. This feature looks like that of Ce₂O₃,²¹ and is quite different from that of CeO₂.¹⁸ So, it is considered that the compounds formed after cleavage of CeSb in air is Ce(III) oxide or its hydroxide. The reaction of CeSb in a vacuum and air is thus written by Eqn (2). Similar reactions have been reported in cerium intermetallic compounds. Cerium is oxidized in air but the transition metals are not.²² The production of Ce(III) by cleavage of CeSb in air contrasts with the production of Ce(IV)

oxide by exposure of Ce metal to 1000 L of oxygen.²³ The light ion sputtering gave state (b), whose Ce 3d and Sb 3d spectral profiles were similar to state (d) in Fig. 4. Further sputtering decreased the O 1s intensity and gave a single peak of Sb 3d.

The chemical shift of Sb in the decomposition layer on LaSb was positive, as mentioned before. On the other hand, the shift of elemental Sb in the decomposition layer on CeSb was negative. Similar negative shifts have been reported for group VIII metals supported by TiO₂^{24–26} and La₂O₃.²⁷ The discussion on the chemical shifts goes beyond the scope of this paper.

The FWHM of Sb 3d in (d) was larger than that of fresh cleaved CeSb surfaces in Fig. 4, where a similar phenomenon was observed in sputtering on LaSb, as mentioned before.

The reaction rate of Eqn (2) on the CeSb surface sputtered by ions was faster than that on the freshly cleaved surface, as shown in Fig. 6. The binding energy of the elemental Sb produced by Eqn (2) in the x-ray photoelectron spectrometer was different from that in the decomposition layer on CeSb cleaved in air.

CONCLUSION

It is well known that rare earth metals are very reactive to many kinds of gases. It was believed that electron spectroscopic studies of rare earth metals need an ultra-high vacuum of below 10^{−8} Pa and that the spectra must be measured within a short time. The lanthanide 3d x-ray photoelectron spectra for the cleaved and fresh surface of LaSb obtained in a vacuum of $\sim 1 \times 10^{-7}$ Pa

coincided with that of the scraped and fresh surface in a vacuum of one order less than that of this experiment. Thus, it is possible to discuss the electronic states in the lanthanide-antimony system by x-ray photoelectron spectra measured within 15 min even in the atmosphere of 10^{-7} Pa when the single crystals are cleaved *in situ*.

The exposure of LaSb and CeSb to a vacuum or air gave lanthanide oxide and elemental antimony. When the oxidation proceeds in air, the antimony becomes an oxide. Although the binding energy of the elemental antimony treated in a vacuum coincided with that of

bulk metal antimony, the binding energies of the element in decomposition layers on the samples cleaved in air shift positively for LaSb and negatively for CeSb.

Acknowledgements

This work was performed at the Laboratory for Developmental Research of Advanced Materials, the Institute for Materials Research, Tohoku University. We would like to express our thanks to Dr A. Donni for reading the manuscript of this paper.

REFERENCES

1. T. Kasuya, Y. Haga, Y. S. Kwon and T. Suzuki, *Phys. B* **186**, 9 (1993).
2. S. Suga, S. Ogawa, H. Nakatame, M. Taniguchi, A. Kakizaki, T. Ishii, A. Fujimori, S. J. Oh, H. Kato, T. Miyahara, A. Ochiai, T. Suzuki and T. Kasuya, *J. Phys. Soc. Jpn.* **58**, 4534 (1989).
3. H. Arai, S. Nakai, T. Mitsuishi, T. Suzuki, H. Ishii, H. Maezawa and M. Tgeshige, personal communication.
4. M. Takeshige, R. Takayama, O. Sakai and T. Kasuya, *J. Jpn. Appl. Phys. Ser. 8*, 129 (1993).
5. S. T. Oyama and G. L. Haller, *Spec. Period. Pept. Chem. Soc. Catal.* **5**, 333 (1981).
6. R. M. Nix, R. W. Judd and R. M. Lambert, *Surf. Sci.* **205**, 59 (1988).
7. H. C. Siegman, L. Schlapbach and C. R. Brundle, *Phys. Rev. Lett.* **40**, 972 (1980).
8. L. Schlapbach, *Solid State Commun.* **38**, 117 (1981).
9. J. Kanamori and A. Kotani (Eds), *Core-level Spectroscopy in Condensed Systems*. Springer-Verlag, Heidelberg (1988).
10. R. Izquierdo, E. Sacher and Y. Yelon, *Appl. Surf. Sci.* **40**, 175 (1989).
11. F. Gurbassi, *Surf. Interface Anal.* **2**, 166 (1980).
12. M. Oku, S. Suzuki, H. Kimura and K. Hirokawa, *Appl. Surf. Sci.* **20**, 549 (1985) and references therein.
13. J. H. Scofield, *J. Electron Spectrosc.* **8**, 129 (1976).
14. Y. Baer, R. Hauger, Ch. Zurcher, M. Campagna, G. K. Wertheim, *Phys. Rev. B* **18**, 4433 (1978).
15. D. F. Mullica, H. O. Perkins, C. K. C. Lok and V. Young, *J. Electron Spectrosc.* **61**, 337 (1993).
16. Y. Iwamino, T. Ishizuka and H. Yamatera, *J. Electron Spectrosc.* **34**, 67 (1978).
17. Y. Takasu, R. Unwin, B. Tesche and A. M. Bradshaw, *Surf. Sci.* **77**, 219 (1978).
18. M. G. Mason, *Phys. Rev. B* **27**, 748 (1983).
19. W.-D. Schneider, B. Delley, E. Wuilloud, J.-M. Imer and Y. Baer, *Phys. Rev. B* **32**, 6819 (1985).
20. M. Takeshige, O. Sakai and T. Kasuya, *Theory of Heavy Fermion and Valence Fluctuations*, ed. by T. Kasuya and T. Sato, pp. 120–133. Springer-Verlag, Berlin (1985).
21. J. C. Fuggle, M. Campagna, Z. Zolnierak, R. Laceres and A. Platur, *Phys. Rev. Lett.* **45**, 1597 (1980).
22. G. Krill, J. P. Kappler, A. Meyer, L. Abadi and M. F. Ravet, *J. Phys. F* **11**, 1713 (1981).
23. G. Strasser, G. Rosina, E. Bertel and F. P. Netzer, *Surf. Sci.* **152/153**, 765 (1985).
24. B. A. Sexton, A. E. Hughes and K. Fogar, *J. Catal.* **77**, 85 (1982).
25. S.-H. Chien, B. N. Shelimov, D. E. Resasco, E. H. Lee and G. L. Haller, *J. Catal.* **77**, 301 (1982).
26. C. C. Kao, S. C. Tsai, M. K. Bahl, T. W. Chung and W. J. Lo, *Surf. Sci.* **95**, 1 (1980).
27. F. Hicks, Q.-J. Yen, A. T. Bell and H. Fleisch, *Appl. Surf. Sci.* **19**, 315 (1984).