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Surface plasmons in NiGa and CoGa alloys

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Abstract

Electron energy losses at the surface of Ga, NiGa and CoGa have been studied by X-ray photoemission spectroscopy (XPS). These features are interpreted as being due to surface plasmons. For Ga metal the experimental result is in good agreement with the surface plasmon energy obtained by a free-electron model. At the surface of CoGa and NiGa alloys, the corresponding energy is about 1 eV higher than that of pure Ga metal. This result is discussed in the framework of a free-electron model as well.

Keywords: Gallium; Plasmons; Polycrystalline surfaces; X-ray photoelectron spectroscopy

1. Introduction

During the past few years many studies of the satellite structure which accompanies the XPS lines of simple and noble metals have been presented [1,2]. However, no detailed results for NiGa and CoGa alloys seem to be available. The satellite structure is generally known to be caused by electrons, which instead of contributing to the main photoemission line have suffered an energy loss by exciting a plasmon or an interband transition. The interpretation of the emission in simple metals can obviously be based on the plasmon model, but the assumption of the free-electron model is not obvious for interpreting the satellites of other metals [3].

One can conceptually distinguish between two plasmon loss mechanisms: energy loss to the bulk plasmons and energy loss to the surface plasmons. It is well known that the bulk plasmons are usually more intense than the surface plasmons in the XPS spectra of simple metals. However, in noble metals this does not seem to be the case [3].

The plasmon energies $\hbar\omega_P$ can be estimated from the experimentally determined dielectric function $\epsilon(\omega)$. For the frequency value ω_P satisfying the equation Re $\epsilon(\omega_P)=0$, we have a bulk plasmon, and Re $\epsilon(\omega_S)=-1$ gives the frequency ω_S of the surface plasmon. The energy of the surface plasmon is usually lower than the energy of the corresponding bulk plasmon. In the free-electron model $\omega_P/\omega_S=\sqrt{2}$.

As far as the background of XPS spectra is concerned, a difficult experimental problem arises from the inevitable electron energy loss satellites which accompanies every photoemission line [4]. It is due to the fact that the absorption length for the incident X-rays is orders of magnitude greater than the escape depth of the photoelectrons which they create. A major fraction of these electrons have lost some energy by exciting a plasmon or

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an interband transition before they leave the alloy. In view of the quantitative analysis it is important to know these phenomena [4].

In this work the importance of surface plasmons is emphasized. The XPS core level spectra of NiGa and CoGa alloys have been investigated using two different take-off angles between the momentum of a photoelectron and the surface plane. Surface plasmons can be identified using a smaller take-off angle.

2. Experimental details

Pure Ga sample was a commercial one with purity better than 99.999%. NiGa and CoGa polycrystalline alloys were prepared by melting the pure metals in an induction furnace containing pure argon gas. Subsequent annealing of the materials for several hours was found to produce an homogenous structure. Rods of NiGa and CoGa alloys were cut to obtain disks of 5 mm diameter and 1 mm thickness and polished with diamond paste. Homogeneity of an alloy was verified by a Perkin-Elmer Phi Model 610 scanning Auger microprobe. Furthermore, a secondary electron image revealed that the sample consisted of crystals with size of 1 mm. Grain boundaries were sharp as well.

XPS data were obtained using a Perkin-Elmer 5400 small spot spectrometer. Specimens were irradiated with a monocromatized Al Kα source ($h\nu$ = 1486.6 eV). The vacuum in the analysis chamber was maintained at 5×10^{-10} Torr. The binding energy of the Au $4f_{7/2}$ line was at 84.0 eV. Spectra were resolved into their Gaussian/Lorentzian components after background subtraction according to the Shirley method. The overall instrumental energy resolution was 0.7 eV.

Sputtering with Ar^+ ions (3 kV, 1.6 μA cm^{-2}) for 20 min decreased the Ga concentration by about 20% in the case of a NiGa alloy. Annealing the sample for 20 min at 750°C in situ reproduced the Ga concentration to the same level as it is for a scraped surface. It turned out that the intensity of a surface plasmon decreased somewhat during those measurements which lasted several hours. The measurements were made at room temperature for NiGa and CoGa alloys, whereas using liquid nitrogen and ethanol the corresponding temperature was −30°C for pure Ga metal.

3. Results

For investigating the plasmons, we have chosen the 2p electrons in metallic gallium. This solid is a nearly free-electron-like metal to which the basic theory should be applicable. The theoretical bulk and surface plasmon energies are sufficiently large, 14.5 and 10.3 eV, respectively [5], so that the contributions of the plasmons are well separated from the main line. Also, the binding energy of the strong Ga 2p line is high enough, whereby the kinetic energy of the photoelectron is not so far from the Cooper minimum, in which the inelastic electron mean free path possesses a smallest value [6]. This makes the experiment more surface sensitive. Fig. 1 shows the $2p_{3/2}$ XPS spectrum of pure gallium metal. The binding energy of the main line is 1116.7 ± 0.1 eV. On the high binding energy side of the main line, electron energy losses are found due to surface and bulk plasmons at 10.4 and 14.4 eV, respectively, which are in excellent agreement with the theoretical free-electron estimates noted above. The binding energy of the 3d band is about 19 eV [7], which explains the absence of interband transitions causing the possible energy shifts. No drastic effects due to core

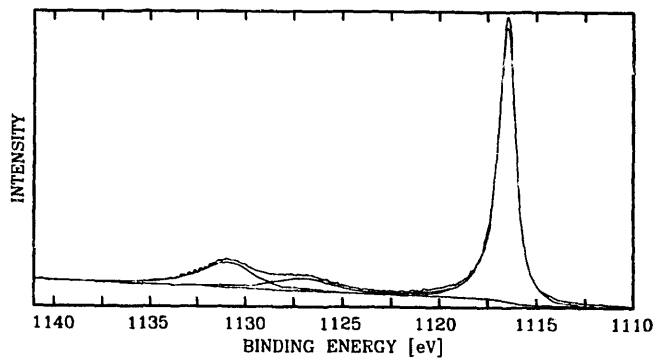

Fig. 1. The $2p_{3/2}$ XPS spectrum of pure gallium metal. The smaller satellite on the high binding energy side of the main line is caused by a surface plasmon. The Shirley background subtraction is also presented. The take-off angle is 45°.

polarization [8] can be expected either, which would reduce the plasmon energy somewhat. Furthermore, the estimated intensities of bulk and surface plasmons relative to the main line are 28% and 17%, respectively.

Turning to NiGa and CoGa alloys, one can note that the Ga $2p_{3/2}$ binding energies are 1116.8 ± 0.1 eV and 1116.7 ± 0.1 eV, respectively. Because the procedure used in the case of the pure Ga metal to extract information about satellites is somewhat arbitrary for the alloys in question, a different approach has been utilized. The measurements have been performed with two different take-off angles 60° and 20° between the direction of the escaping photoelectron and the surface. The spectrum found by the latter angle is more surface sensitive than that obtained by the former one. Subtracting the former spectrum from the latter one it is possible to separate the electron energy loss at the surface relative to that of the bulk. This result is shown in Fig. 2 for NiGa and CoGa. The inset denotes the difference between the "surface" and the "bulk" contributions. The binding energy of this feature is 1128.2 ± 0.2 eV, which gives an energy loss of about 11.4 eV and a relative intensity 21.2% for a NiGa surface. In the same way, the corresponding electron energy loss is about 11.3 eV and the intensity ratio relative to the main line is 19.6% for a CoGa alloy. These results have been obtained by sputtering the surface of an alloy with Ar^+ ions for about 15 min and then annealing at 750° for about 15 min during repeated cycles. Thereafter, the XPS measurements have been made at room temperature. It is evident that the surface satellite structure of the Ga $2p_{3/2}$ line of NiGa and CoGa alloys has a higher binding energy than that of a Ga metal.

In order to consider the influence of the treatment of the surface upon these electron energy losses, scraping of the surface has been performed at room temperature as well. Although there is an energetic coincidence of the features of NiGa in both cases, the scraped surface exhibits a smaller intensity difference between the surface and bulk sensitive spectra. This effect may largely arise from a more rough surface of the scraped specimen if one compares with that of the sputtered and annealed specimen.

Fig. 3 describes the similar situation as in Fig. 2, but now for pure Ga metal. One can note that the second surface plasmon with a larger loss energy can be identified as well. Furthermore, the

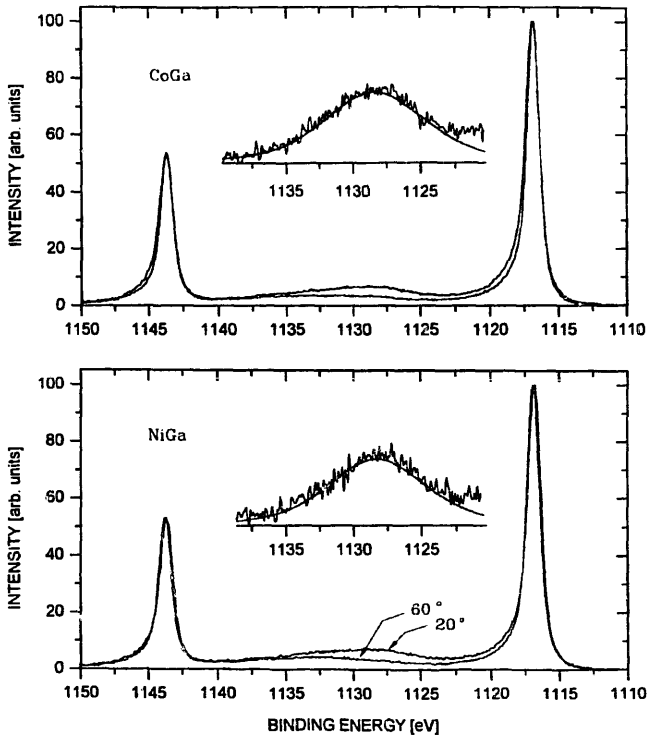

Fig. 2. The 2p spectra of Ga in the NiGa and CoGa alloy. The inset gives the surface satellite, which is found by subtracting the bulk sensitive spectrum (60°) from the surface sensitive spectrum (20°). The spectra are normalized at the main lines.

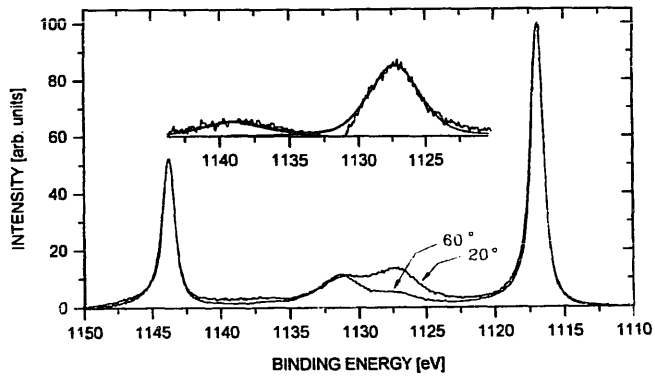

Fig. 3. The similar spectra as in Fig. 2, but now from the scraped Ga metal surfaces. The intensity difference between the "surface" and "bulk" spectra describes the main contribution to the surface plasmons.

extracted intensities of the first surface plasmon and the second surface plasmon satellite relative to the Ga $2p_{3/2}$ main line are about 23.5% and 6.6% and the energies 10.5 and 22 eV, respectively.

The Ni 2p core-level spectra of the NiGa alloy have also been considered. The intrinsic "hole" satellite appears at about 6 eV on the high binding energy side below the main line [9], which is characteristic of nickel in the sense that the d-band is not fully occupied in the ground state. This satellite turns out to be bulk sensitive because for a small take-off angle (20°) only the background of the spectrum is enhanced (which is largely caused by surface plasmons) and the essential features of the satellite remains the same as for that of a large take-off angle (60°). This suggests that the "hole" satellite does not considerably depend on the neighbouring surface atoms of the core-ionized atom.

In Fig. 4 the corresponding Ni 2p XPS spectra of the NiGa alloy can be seen with these two different take-off angles. Also the background has been subtracted. In this case, the obtained intensity of the surface plasmon satellite relative to that of the Ni 2p main line is about 4%, which is much less than 21.2% obtained for the Ga 2p spectrum of the alloy. The weakness of the extracted surface feature in Fig. 2 suggests that the main contribution to the surface plasmon satellite arises from the sudden creation of the Ga 2p core-hole in the alloy, whereby this satellite would be largely an intrinsic one. One should note, however, that the weaker relative intensity of the surface plasmon satellite for the Ni 2p spectrum can be to some extent ascribed to the about 264 eV lower binding energy of the core-level if one compares with that of the Ga 2p line. This effect for the Ni spectrum is due to the longer electron mean free path caused by the Cooper minimum.

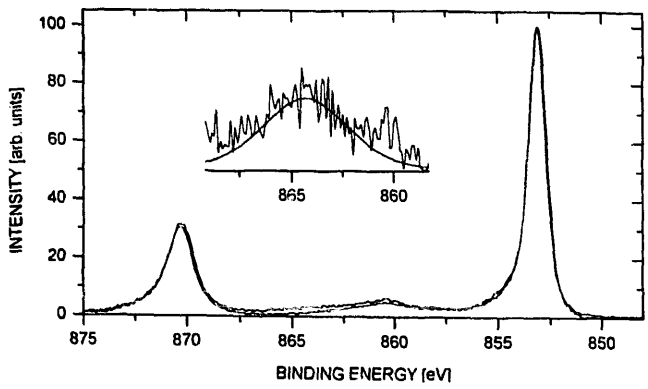

Fig. 4. The extracted surface plasmon satellite for the Ni $2p_{3/2}$ spectrum of the NiGa alloy.

4. Discussion

There are some discrepancies concerning the Ga main lines in Fig. 3. The surface sensitive main line turns out to be somewhat broader than the bulk sensitive one in these alloys. Also, the tailing behaviour on the high binding energy side of the surface sensitive peak seems to be more pronounced. It is evident that the line broadening in question arises to some extent from the surface–atom core-level shift, although this effect is usually assumed to be small [10]. Nevertheless, we feel that the small influence of the shape of the main line on the satellite structure does not affect the interpretation of the surface features.

In order to discuss the surface features of alloys it is worthwhile to consider the optical constants of pure Ni and Co metals [11]. For Ni, Re $\epsilon(\omega)$ is quite similar to that of Ag, whereas for Co the corresponding behaviour of the dielectric function is more free-electron-like. The damping effect can be ascribed to Im $\epsilon(\omega)$, which shows a decreasing trend in going from 0 to 120 eV. The lifetime contribution Im $\epsilon(\omega)$ arises largely from interband transitions and reduces the intensity of the bulk plasmons. Nevertheless, in the case of $Ni_{50}Ga_{50}$ and $Co_{50}Ga_{50}$ alloys, the free-electron calculation gives the energies 17.0 and 12.0 eV for bulk and surface plasmons, respectively. This energetic coincidence is largely due to the similar lattice parameters for these alloys (Appendix A). For NiGa the corresponding experimental energies are about 15.7 and 11.4 eV and CoGa possesses almost identical loss energies. The free-electron estimates are just slightly larger than the experimental energies.

A reduction of the energy of a plasmon by the interband transition, which involves a one-electron transition between the two bands, is to be expected if the calculated plasmon energy of the free-

electrons in the conduction band is at least comparable to the binding energy of some tightly bound electrons [5] (for example the interband transition from the Ni 3d band above the Fermi-level in the case of a NiGa alloy). It is therefore likely that the energy of the surface plasmon would be shifted towards a slightly lower value as well. Also, a damping effect caused by Im $\epsilon(\omega_s)$ would diminish the intensity of a surface plasmon in the case of an alloy.

The full width at half maximum (FWHM) values of the slightly asymmetric Ga $2p_{3/2}$ lines are about 0.84 and 1.06 eV for the pure metal and the alloys, respectively. The corresponding FWHM energies for surface plasmon satellites are about 5 and 9 eV. One can note that these surface features of the alloys are almost twice as broad as that of the pure gallium metal, although the areas of the satellites relative to those of the Ga $2p_{3/2}$ lines are very similar (about 20%).

There have been suggestions that for diffuse surfaces the corresponding plasmon energies can be slightly changed [12]. However, in our case it was observed that the main effect of the scraped surface was just to reduce the intensity ratio between the surface plasmon satellite and the main line.

As a conclusion we can note that the electron energy losses at the surface of NiGa and CoGa alloys are about 11.4 and 11.3 eV, respectively. These features are suggested to be caused by surface plasmons. The overall agreement between experiment and free-electron theory is good as far as plasmon energies are concerned. The broadening of satellites in question are explained to be due to interband transitions. Furthermore, the surface plasmon seems to be largely an intrinsic satellite of the Ga 2p main line for the XPS spectra of these alloys.

Appendix

The surface plasmon energy of a binary alloy can be estimated in terms of the free-electron model by calculating first the density of valence electrons [13]

$$\eta = 6.02 \times 10^{23} \frac{Z\rho}{A}, \tag{A.1}$$

where Z is the number of valence electrons of the molecule, ρ is the density of an alloy (g/cm^3) and A is the molecular weight of the molecule in question. The density ρ can be obtained for a simple cubic crystal from

$$\rho = \frac{n}{V}\frac{A}{N}, \tag{A.2}$$

where n is the number of molecules in the volume V of the primitive cell and N is equal to 6.02×10^{23} molecules/mol. In our case, the NiGa and CoGa alloys have the cesium chloride structure [14] with one molecule per primitive cell. The volume is now $V = a^3$, where the lattice parameters are $a = 2.88$ and 2.87 Å for NiGa and CoGa alloys, respectively [14]. The numbers of valence electrons for Ni, Co and Ga atoms are 2, 2 and 3, respectively. The bulk plasmon energy $\hbar\omega_P$ is of the form

$$\hbar\omega_P = \sqrt{\frac{4\pi e^2 \eta}{m}}, \tag{A.3}$$

where m is the mass and e is the charge of an electron. The surface plasmon energy is

$$\hbar\omega_S = \frac{\hbar\omega_P}{\sqrt{2}}. \tag{A.4}$$

Hence, (A.3) and (A.4) give the same surface plasmon energy 12.0 eV and the bulk plasmon energy 17.0 eV for NiGa and CoGa alloys.

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