Resonant photoemission in Cr silicide at the absorption energy $\text{Cr } 2p$

L. Galán and M. García

Departamento de Física Aplicada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain

J. M. Ripalda

Instituto de Microelectrónica de Madrid CSIC, Isaac Newton 8, E-28760 Tres Cantos, Spain

I. Montero^{a)} and E. Román

Instituto de Ciencia de Materiales de Madrid, CSIC, E-28049 Madrid, Spain

D. R. Batchelor and P. R. Bressler

BESSY, Albert Einstein Strasse 15, D-12489, Berlin, Germany

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Valence band photoemission has been measured in chromium silicide as a function of the photon energy near the $\text{Cr } 2p^{3/2}$ absorption threshold. Evidence of resonant photoemission is observed for the $3d$ valence band and the two-hole satellite. The threshold for normal Auger regime is 2.8 eV below the absorption peak and 0.8 eV below the $\text{Cr } 2p^{3/2}$ binding energy, even lower than in pure Cr metal where it is already at extreme levels. The requirement for good resolution in photon energy relative to absorption width for the resonant Raman Auger to be observed is found to be less restrictive than expected. © 2004 American Institute of Physics. [DOI: 10.1063/1.1758779]

In long-term research on surface coating materials to prevent multipactor effect in high-powered rf in communication and surveying equipment in spacecraft,¹ we chose to study Cr silicides because of their low secondary electron emission yield and their resistance to deterioration upon air exposure. Multipactor effect is an electron discharge in vacuum in resonance with the rf field that is fed back by secondary electron emission on the exposed surfaces.^{1,2} In order to study the electronic structure of these materials in relation to these properties, we have performed valence band photoemission spectroscopy near the high-energy $\text{Cr } 2p_{3/2} \rightarrow 3d$ absorption threshold, which is known to exhibit unexpected resonance effects in the pure metal.³

Resonance photoemission spectroscopy is not only of interest as a technique for studying the electronic structure,⁴ but is also of fundamental interest in itself. Although it is a well-established technique, many questions remain unclear, such as: the condition of quasistationary intermediate states, the relation to resonance of related Auger transitions and two-hole satellites, and the requirement of high resolution in photon energy for the resonant Raman Auger to take place.^{5–7} Here, we report experimental observations pertaining to the complexity of some of these questions. These effects were not detected in previous photoemission spectroscopic studies of Cr silicides at lower photon energies.^{8,9}

Very thin silicide films were prepared in nearly ultrahigh vacuum (10^{-9} mbar range) by sublimation of Cr onto Si (100) substrates followed by rapid annealing (1000 K, 90 s) in the preparation chamber of the experimental station. The proportion of oxide species of Si or Cr were below 10% as measured in $\text{Si } 2p$ and $\text{Cr } 3p$ and $2p$ core level spectra. Cr–Si reaction was indicated by changes in valence band structure⁹ and $\text{Si } 2p$ chemical shifts. Valence band structures and core level intensities also indicated that CrSi_2 silicide

formation resulted from this preparation technique.

Photoemission spectroscopy was performed *in situ* at the PM-1 beam line of BESSY II, with the SX-700-I monochromator and a large throughput angle-resolved electron-energy analyzer (Phoibos, SPECS, Germany). Resolution of the monochromator at the high energies of interest (~ 580 eV) was ~ 1.7 eV, while that of the analyzer was ~ 0.5 eV. Photoemission spectroscopy was recorded in the energy distribution curve (EDC) or photon energy constant, but also constant initial state or binding energy constant (CIS) and constant final state (CFS) or kinetic energy constant modes. Thus, a map of normalized photoemission intensity as a function of photoelectron and photon energies was obtained.

Before resonance, the valence band spectra, which have a typical line shape for $h\nu = 571$ eV (PE) presented in Fig. 1(b), show structures mainly due to Cr $3d$, Si $3s$, and O $2s$ orbitals (absorption, contamination). Resonance enhancement of the Cr $3d$ valence levels appeared at 575.8 eV photon energy (PE), while the $\text{Cr } L_3$ absorption peak in x-ray absorption spectroscopy (XAS) is at 576.3 eV PE³ and $\text{Cr } 2p_{3/2}$ core level at 574.3 eV binding energy (BE) in x-ray photoemission spectroscopy (XPS, $h\nu = 700$ eV), as in the pure metal. However, resonant enhancement was not as pronounced as in the pure metal, $\times 2.5$ compared to $\times 20$. A typical spectrum above resonance ($h\nu = 579$ eV) is also depicted in Fig. 1(a). Besides the photoemission features mentioned above, it also shows easily identified Auger structures because they appear at constant kinetic energy (KE). The intense peak at 570.3 eV KE is due to $\text{Cr } L_3VV$ Auger emission (labeled A and A1 in spectrum *a*). The Auger spectrum was fitted with the calculated line shape shown at the bottom of Fig. 1, corresponding to threshold. This line shape is formed by two Lorentzian peaks and a Shirley-type background with only a shape parameter controlling the widths. The energy position, width, and height of the peaks were: E_1 , w_1 , h_1 , $E_2 = E_1 - 21.35$ eV; $w_2 = 1.96w_1$, and h_2

^{a)}Electronic mail: imontero@icmm.csic.es

FIG. 1. EDC for resonant photoemission in chromium silicide: Typical spectra for above (a) and below (b) resonance photon energies; (SiCr_x vb) valence band spectrum with Auger signal subtracted; (RRA Sat.) resonant Raman Auger/two-hole satellite=(b), (c); and (Auger) calculated Auger spectrum at resonance.

$=0.358h_1$, respectively. The constant in the integral of the Shirley-type background was 0.050 eV^{-1} . To fit experimental data, it was only necessary to adjust its intensity h_1 and to modify slightly its KE position E_1 and its width w_1 . At threshold, they were $E_1=570.0 \text{ eV KE}$, $w_1=4.42 \text{ eV}$, while for normal Auger, $E_1=570.3 \text{ eV KE}$, $w_1=4.89 \text{ eV}$. For decreasing photon energy, the Cr Auger emission converges towards the resonant Raman Auger (RRA) satellite. Usually, the valence band peak, the Auger, and the RRA satellite converge at the same energy. In this case, it can be observed in Fig. 2 that in the silicide the Cr Auger emission converges towards Cr 3d after 2.3 eV has passed the resonance at 575.5 eV (Fig. 3) and 2.5 eV has passed the absorption peak, to finally reach a threshold at 3.5 eV BE, while the Cr 3d band peaks at 1.8 eV BE, see Fig. 2. In addition, this abnormal behavior is maintained almost 1 eV PE further than in the pure metal.³ This is because the Cr Auger kinetic energy is $\sim 0.5 \text{ eV}$ less than in the pure metal, indicating less metallic character for the silicide (i.e., smaller extra-atomic relaxation energy).

The result of subtracting the Auger emission from valence band spectra above resonance is presented in Fig. 1 as SiCr_x vb (an average spectrum). This line shape is in agreement with spectra measured at $\sim 200 \text{ eV PE}$, very far from the resonance and with much better resolution and statistics. However, this line shape is notably different from the spectra just below resonance. A different spectrum is presented in Fig. 1 as RRA Sat., which is undoubtedly identified as the resonant Raman Auger equivalent to the two-hole satellite since it has the same line shape as the Auger emission but appears at constant 3.5 eV BE. In Fig. 3 the resonant Raman Auger/two-hole satellite can be found to reach down to $\geq 7 \text{ eV}$ below the absorption peak. The appearance of the radiationless resonance Raman effect is an indication of resonant

FIG. 2. Resonant Auger: Position of the Auger maxima as a function of photon energy and binding energy. The position of main structures are represented as well as the width (dotted lines) of Auger signal. The position of the Cr absorption peak and core level binding energy are also marked.

photoemission. In this case, the intensity enhancement of the 3d band at resonance should not be due to simple addition of the overlapping Auger signal. This is demonstrated in Fig. 4, where a CIS spectrum for $0.5 (\pm 0.5) \text{ eV BE}$ is presented (obtained from EDCs integrating the signal in 1 eV interval centered at 0.5 eV BE), together with that resulting from subtraction of the Auger signal. The 3d resonance occurs 0.6 eV after the absorption peak and clearly after the resonance of the Auger signal, Fig. 3, indicating that there is interference between the Auger and photoemission signal and not just addition. However, no destructive interference (usual Fano line shape) was easily observable before the resonance

FIG. 3. Intensity of the normal Auger and resonant Raman Auger: Intensity values correspond to the Cr Auger line in the map of Fig. 2.

FIG. 4. L_3 -XAS-edge Cr $3d$ resonant photoemission: Constant initial state spectra of Cr $3d$: Contribution of the Cr Auger signal and the resonant Raman satellite have been subtracted from the lower spectrum.

peak, contrary to the case for the low-energy Cr $3p$ absorption threshold in the pure metal.¹⁰

The intensity along the Auger (Fig. 3) and the $3d$ lines (Fig. 4, bottom spectrum) should be convoluted with the third (SiCr, vb) and the last (Auger) spectra of Fig. 1, respectively, in order to get the complete map of the photoemission signal. The final image is depicted in the PE-BE map of the photoemission structures (Fig. 2).

It is generally assumed that the resolution in photon energy must be very good compared to the absorption line width if the resonant Raman Auger satellite is to occur.^{3,7} In our case, resolution of the photon channel (~ 1.7 eV) was poor but probably still below the limit (~ 3 eV for absorption, as measured by the Auger CFS, Fig. 3), because in spite of this all the characteristics of the phenomenon were there.

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