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The Ag $M_5N_{45}N_{45}$ Auger photoelectron coincidence spectra of disordered $Ag_{0.5}Pd_{0.5}$ alloy

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Abstract

An effect of disorder broadening (DB) on the Ag $M_5N_{45}N_{45}$ Auger spectra in the random substituted $Ag_{0.5}Pd_{0.5}$ has been investigated by Auger photoelectron coincidence spectroscopy (APECS). Data were collected for the Ag $M_5N_{45}N_{45}$ Auger line coincident with the Ag $3d_{5/2}$ photoelectron line (and its higher and lower binding energy sides). It is shown that the broadening of the Ag $M_5N_{45}N_{45}$ line is directly associated with the presence of disorder broadening of the Ag $3d_{5/2}$ photoelectron line. The APECS experiment is used to demonstrate the broadening in a novel way.

Keywords: Silver–palladium alloy; Auger photoelectron coincidence spectroscopy; Photoelectron spectroscopy; 4d transition metal; Disorder broadening

1. Introduction

In recent years, the effect of disorder on the electrostatic energy in disordered alloys has attracted attention. Studies of local potential due to Madelung contributions [1,2] on atom sites in disordered alloys were carried out by Cole and Weightman [3,4]. The Charge Correlated Model (CCM) indicated that the disorder broadening of the core photoelectron lines of Cu 2p in CuPd, CuPt and CuZn alloys

occurred with the spread of local potential in the atomic cores arising from the effects of charge transfer [2–5]. The theoretical model predicted the composition dependence of the full width at half maximum (FWHM) of core XPS for CuPd alloys. The FWHM of Cu 2p increases by 0.23 eV from pure Cu to $Cu_{0.5}Pd_{0.5}$[4], due to the contribution of the change in site potentials in the disordered alloy. The first observation of disorder broadening of the core level photoelectron line of Cu from a substitutional disordered alloy of CuPd was shown in Ref. [6]. A series of subsequent experimental results for CuPt and CuPd indicated the broadening to be greatest for equiatomic composition, e.g. $Cu_{0.5}Pt_{0.5}$ and $Cu_{0.5}Pd_{0.5}$[4,7].

Ag_xPd_{1-x} is a binary alloy with strong disorder. The d-bands of the constituents overlap to a large extent while the center of the band is almost independent of the concentration for Ag as well as for Pd [8,9]. In this alloy, the d-bands are full and the alloy shows no magnetic behavior. From an electronic point of view, the AgPd system is very similar to the CuPt and CuPd systems. Auger electron spectra originating from decay processes of a deep core hole into two valence band holes tend to show some sensitivity to the surroundings. Pure Ag and Pd have been widely investigated by XPS and AES. The Ag $M_5N_{45}N_{45}$ Auger spectrum shows an atomic-like shape with multiplet structure. In pure Pd, the $M_5N_{45}N_{45}$ spectrum is also essentially quasiatomic, although considerably less sharp than in Ag [10].

Auger photoelectron coincidence spectroscopy (APECS) has been employed to investigate the correlations between Auger electrons and photoelectrons for many years [11,12]. In the APECS experiment, two electron analyzers are used to examine the electron energy distribution coming from a surface excited by X-ray irradiation. One analyzer remains fixed at a given energy, usually that of the photoelectron, while the second analyzer is swept through the energy range of the corresponding Auger line. The only events counted are those where both the photoelectron and the associated Auger electron are detected. This is accomplished using analyzers with very good timing resolution. In this way, it is possible to simplify the spectrum by separating those parts that include a particular core level and therefore determine the origin of particular features in the Auger spectra. It is also possible to reverse the experiment and determine which photoelectron lines correspond to different parts of the

Auger spectra by fixing the energy of the Auger analyzer and sweeping the photoelectron spectrometer. By using the APECS facilities, a number of research groups recorded high resolution Ag $M_5N_{45}N_{45}$ Auger spectra coincident with Ag $3d_{5/2}$ and Ag $3d_{3/2}$ photoelectron lines [13,14]. Recently we have studied the effect of disorder broadening of core level photoelectron line on the Ag $M_5N_{45}N_{45}$ Auger spectra in random substituted $Ag_{0.5}Pd_{0.5}$ alloy using APECS. Data were collected for the Ag $M_5N_{45}N_{45}$ Auger line coincident with the Ag $3d_{5/2}$, as well as the higher and lower binding energy sides of the peak of the photoelectron line.

2. Experimental

The APECS apparatus used to make these measurements has been described previously [15]. A detailed description of the method used to obtain the coincidence data and conventional single spectra from random coincidence background in APECS is given by Thurgate [16]. $Ag_{0.5}Pd_{0.5}$ polycrystalline solid solution samples were obtained from P. Weightman (the same material as used in Ref. [17]). They had been prepared by melting high-purity Ag and Pd together under argon in an ARC furnace followed by rapid quenching. The sample was repeatedly remelted to ensure homogeneity. Composition was determined by weighing the Ag and Pd and noting that there was no loss of weight during melting and confirmed by high resolution XPS. During the APECS experiment, the sample surface was cleaned each day by in-situ mechanical scraping with a tungsten carbide blade. After about 22 h of data collection, no oxygen or carbon contamination was found. The AgPd single and coincidence spectra were collected using a Mg Kα X-ray (1253.6 eV) source. A pair of hemispherical sector analyzers (HSA) were each operated at a constant pass energy of 135 eV, giving an analyzer energy resolution of 2.2 eV. The scanning analyzer was swept through the energy range of the Ag $M_5N_{45}N_{45}$ Auger line 10 times each day in order to ensure that the spectra were free from any artifact due to increasing contamination after cleaning while the other energy analyzer was fixed at the photoelectron line. Both 'single' (i.e. regular Auger spectra) and coincidence data have been derived from the same data set with the same energy scale. The single spectra data come from summing all

electrons detected by the scanning analyzer regardless of what time they arrived, whereas the coincidence data come from counting only those electrons that arrived coincident with an electron from the other detector. We collected the Ag $M_5N_{45}N_{45}$ spectrum coincident with the Ag $3d_{5/2}$ line at its peak position of 886.0 eV (kinetic energy) detected by the APECS. The measurements were repeated by setting the photoelectron analyzer at the kinetic energies (KE) of 885.2 and 886.8 eV, where the intensities are 75 and 70% of the intensity at peak position (886.0 eV), respectively. It has been shown [4] that the core level binding energy of a B atom surrounded by all A atoms in an AB alloy shifts in the opposite direction to that observed for a B impurity in an A host. The low kinetic energy side experiment (KE=885.2 eV) is expected to enhance the signal from Ag atoms with a higher than average number of Pd neighbors. Each spectrum took about 3 weeks to acquire.

High resolution Ag $M_5N_{45}N_{45}$ and core level and valence band of XPS spectra of $Ag_{0.5}Pd_{0.5}$, Ag and Pd were obtained with a Kratos-Axis Ultra spectrometer using monochromated Al Kα (1486.6 eV) radiation. The pass energy, the resolution of the energy analyzer and the energy step for data acquisition were 10 eV, 0.059 and 50 meV, respectively. These measurements were used to accurately determine the energy positions of the lines reported here.

3. Results and discussion

3.1. XPS/AES experimental results

Figs. 1–3 show the high resolution XPS/AES of Ag 3d, valence band structure and Auger lines, respectively, in Ag, $Ag_{0.5}Pd_{0.5}$ and Pd. The line positions of interest are summarized in Table 1. The FWHM of Ag $3d_{5/2}$ increases from 0.59 eV in pure Ag to 0.68 eV in $Ag_{0.5}Pd_{0.5}$. The difference between them, 0.09 eV, is less than that of $Cu_{0.5}Pd_{0.5}$ [4]. This implies that a similar effect of change in the site potential on the core photoelectron line exists in AgPd alloy such as that in the other alloys, e.g. CuPd, CuPt, etc. Weightman [18] has carried out more accurate determinations which show the FWHM of the Ag $3d_{5/2}$ line in pure Ag to be 0.51 eV and the result for $Ag_{0.5}Pd_{0.5}$ alloy to be 0.58 eV. These results compare well with our estimates and are accurate to better than 0.01 eV. The asymmetry

in the Ag 3d (increase in intensity in the low kinetic energy side, see Fig. 1) with increase in Pd concentration is recognized as the Pd contribution [4].

Fig. 2 shows the valence band structures. For the pure Ag (dotted line in Fig. 2), the large peaked structure above 3.7 eV corresponds to the 4d band and the flatter structure at lower energies to the 5s conduction band. However the main structure associated with the 4d band of Pd (dashed line in Fig. 2) sits on top of the Ag sp band, well separated from the Ag d band and partly overlapping with the Ag 5s conduction band. The screening of the d electrons of Ag and Pd is considerable and the nature of an isolated Ag ion in a Pd matrix is still quite atom-like, as far as the 4d electrons are concerned. The Ag $M_5N_{45}N_{45}$ Auger line of $Ag_{0.5}Pd_{0.5}$ shifts by about 0.3 eV toward higher kinetic energy (Fig. 3). This is because of a considerable admixture between the Ag 4d and Pd 4d density of state (DOS) over the whole of the d band. The disorder broadening effect on the $M_5N_{45}N_{45}$ Auger line of Ag is quite clearly shown in Fig. 3. The FWHM of the Ag $M_{45}N_{45}N_{45}$ Auger line increases from 3.26 eV in pure Ag to 3.54 eV in $Ag_{0.5}Pd_{0.5}$ alloy.

3.2. APECS experimental results

For comparison with the Auger coincidence spectra of $Ag_{0.5}Pd_{0.5}$, we repeated the APECS experiment of Ag $M_{45}N_{45}N_{45}$ coincident with Ag $3d_{5/2}$ from the clean surface of pure Ag as shown in Fig. 4. The dotted line with error bars is the coincidence spectra, while the solid lines represent the single spectrum data. Fig. 4 shows that the $3d_{5/2}$ coincidence spectrum of the main two-hole Ag $M_5N_{45}N_{45}$ component is free from any intensity contributed from the overlapping M_4NN and M_3VV Auger lines. The $3d_{5/2}$ coincidence spectrum of Ag agrees well with the single spectrum peak in the region of the $M_5N_{45}N_{45}$ peak. In Fig. 4, the intensity of the low energy tail of the coincidence spectrum is not significantly reduced compared to the single spectrum. That is because there is no significant three- or four-hole final states resulting from shake-up/off processes.

Now we discuss the APECS experimental result from the disordered $Ag_{0.5}Pd_{0.5}$ alloy. Fig. 5 is the Ag $M_5N_{45}N_{45}$ Auger spectrum coincident with Ag $3d_{5/2}$ at its peak position of 886.0 eV (KE). The solid line is the regular single spectrum data, while the dashed line with error bars is the coincidence signal

derived from the same data set. The line widths of single spectrum of Ag $M_5N_{45}N_{45}$ in pure Ag (Fig. 4) and AgPd (Fig. 5) obtained by APECS are much wider than that of the high-resolution spectra by Kratos-Axis Ultra spectrometer (Fig. 3), due to the higher energy resolution of the Kratos instrument. The APECS instrument must be run under conditions of high collection efficiency which requires a relatively high pass energy, and consequent poor energy resolution. The FWHM of Ag $3d_{5/2}$ and Ag $M_5N_{45}N_{45}$ obtained using Kratos and APECS instruments are listed in Table 1. A question is whether it is possible to measure those photoelectrons with binding energy affected by the disorder broadening due to the relatively small magnitude of the effect using an energy analyzer with a limited resolution. In order to answer this question, a simple simulation was carried out. In Fig. 6, four plotted Gaussian lines approximately represent the Ag $3d_{5/2}$ line in pure Ag obtained by Kratos (solid line; Peak I), the Ag $3d_{5/2}$ line in $Ag_{0.5}Pd_{0.5}$ alloy obtained by Kratos (dashed line; Peak II), the Ag $3d_{5/2}$ line in $Ag_{0.5}Pd_{0.5}$ centered at the peak +0.8 eV obtained by APECS (dotted line; Peak III), and the Ag $3d_{5/2}$ line in $Ag_{0.5}Pd_{0.5}$ centered at the peak −0.8 eV obtained by APECS (dotted line; Peak IV). The first peak (peak I) represents the emission from pure Ag. The second peak (peak II) represents emission from the disordered broadened alloy. The overlap with the first two peaks of the third peak (peak III) indicates the contribution to the measured signal made when the analyzer is +0.8 eV above the peak energy, while the overlap of the fourth peak (peak IV) with the first two peaks indicates the contribution to the signal when the analyzer is positioned below the peak.

Consider the case when the analyzer is centered below the center energy. The dark shading shows the contribution to the signal from atoms where charge transfer has resulted in a significant shift in their binding energies. As can be seen, the relative proportion of those that have a lower kinetic energy is greater than those with a higher kinetic energy. So we predict that a bias in the distribution of the disorder broadening affected core level photoelectron binding energies can be introduced by positioning the analyzer above or below the centroid of the photoelectron line as shown in Fig. 6 (i.e. the difference in area of the shaded regions on either side of the photoelectron peak). In effect then, a different distribution of atomic sites is sampled and the coincident Auger spectrum is expected to reflect this.

In Fig. 5, a least squares algorithm was used to shift the single spectra and find the position where it best coincided with the peak in the coincidence spectra (dashed line). The coincidence spectrum appears narrowed on both sides of the peak and the peak position is almost unshifted from the single spectral position. When the fixed analyzer moves to the high kinetic energy side by 0.8 eV, i.e. KE=886.8 eV, the Ag $M_5N_{45}N_{45}$ Auger coincidence spectrum shifts to the low kinetic side by −0.39 eV, while the peak position of the single spectrum is unshifted (Fig. 7). Fig. 8 shows the Ag $M_5N_{45}N_{45}$ Auger coincidence spectrum while the fixed analyzer is located at 885.2 eV. It is clearly shown that the coincidence spectrum becomes broadened on the high kinetic side. The peak position of the coincidence spectrum shifts to 352.57 eV (see the dashed line in Fig. 8), which is 0.47 eV from the single spectrum line (or reference line). From Figs. 5, 7 and 8, we find that all the single spectrum data, regardless of the fixed photoelectron line position, are almost the same and much broader than that from pure Ag (refer to Fig. 4). This may be due to the increase in the density of states near the Fermi level with the increase in Pd concentration so that $[4d^2] \rightarrow [4d^1V^2]$ transitions, where V^2 represents a two-hole state near the top of the conduction band [17], might be important in determining the Auger profiles. The shift in coincidence spectra clearly indicates that the broadening of Ag $M_5N_{45}N_{45}$ from $Ag_{0.5}Pd_{0.5}$ alloy is directly associated with the disorder broadening of the core level photoelectron line, i.e. Ag $3d_{5/2}$, and d-band structures well overlapping each other.

4. Conclusion

The FWHM of Ag $3d_{5/2}$ increases from 0.59 eV in pure silver to 0.68 eV in $Ag_{0.5}Pd_{0.5}$ alloy. This disorder broadening of the Ag 3d core line is due to the spread of local potentials in the atomic cores arising from the effects of charge transfer. The APECS experiment indicates the broadening of Ag $M_5N_{45}N_{45}$ Auger line of $Ag_{0.5}Pd_{0.5}$ alloy is associated with the disorder broadening of the core level photoelectron line and it is due to the significant overlap of Ag and Pd d-band structures.

Acknowledgments

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Fig. 1. Comparison of XPS Ag 3d spectra of Ag with $Ag_{0.5}Pd_{0.5}$. Measurements were made with a high resolution Kratos-Axis Ultra monochromated spectrometer. The energy scale of the $Ag_{0.5}Pd_{0.5}$ spectrum has been shifted by −0.5 eV in order to coincide with the pure Ag spectrum.
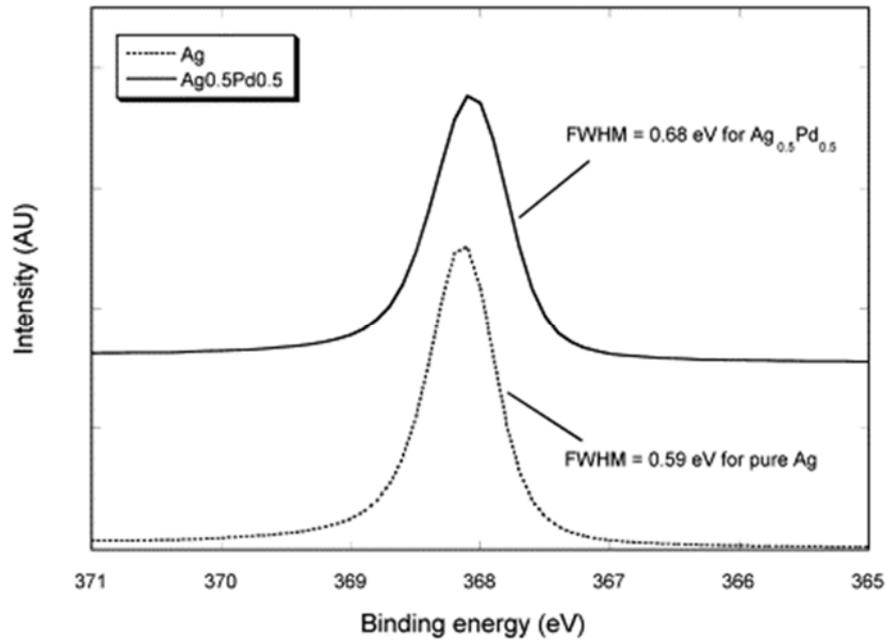
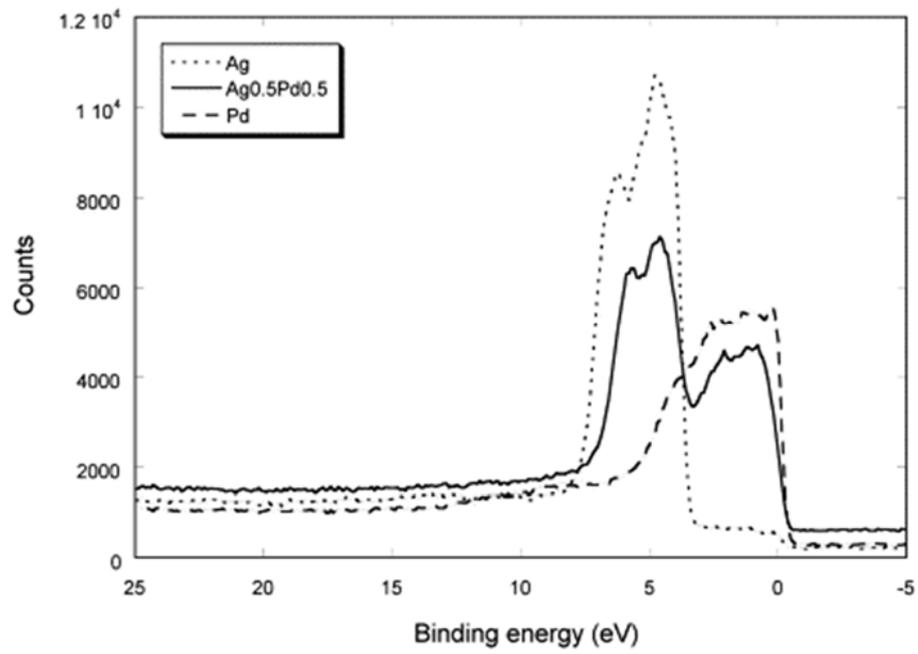Fig. 2. The XPS valence band spectra of pure Ag (dotted line), $Ag_{0.5}Pd_{0.5}$ (solid line) and Pd (dashed line).

Fig. 3. Comparison of Ag $M_{45}N_{45}N_{45}$ Auger spectra of Ag (dotted line) with $Ag_{0.5}Pd_{0.50}$ (solid line). The energy scale of the pure Ag spectrum has been shifted by +0.2 eV in order to coincide with the $Ag_{0.5}Pd_{0.5}$spectrum.
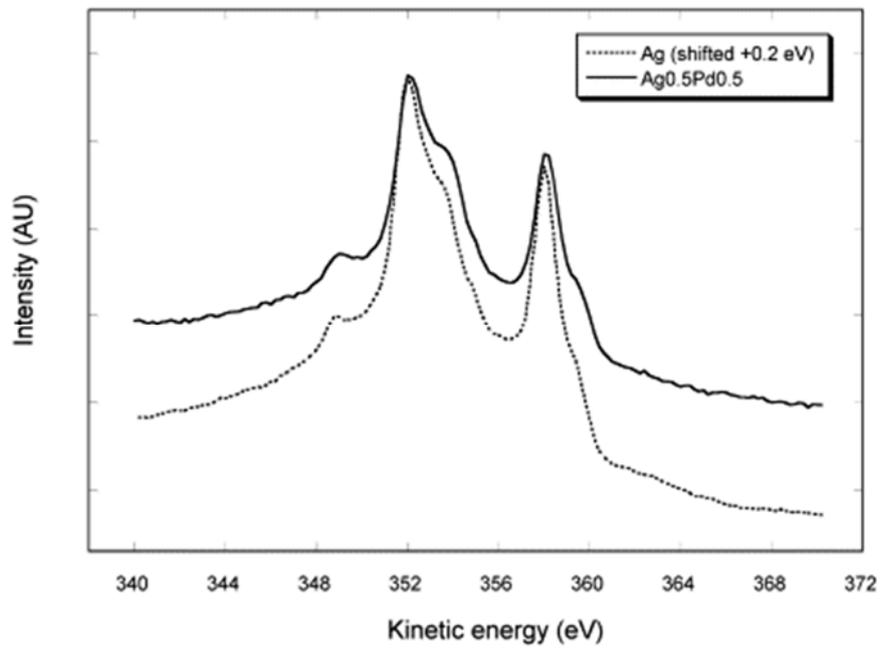
Fig. 4. The Ag $M_5N_{45}N_{45}$ Auger spectrum coincident with Ag $3d_{5/2}$ for pure Ag. The solid line gives the regular single spectral data and the dotted line with error bars represents the coincidence data.
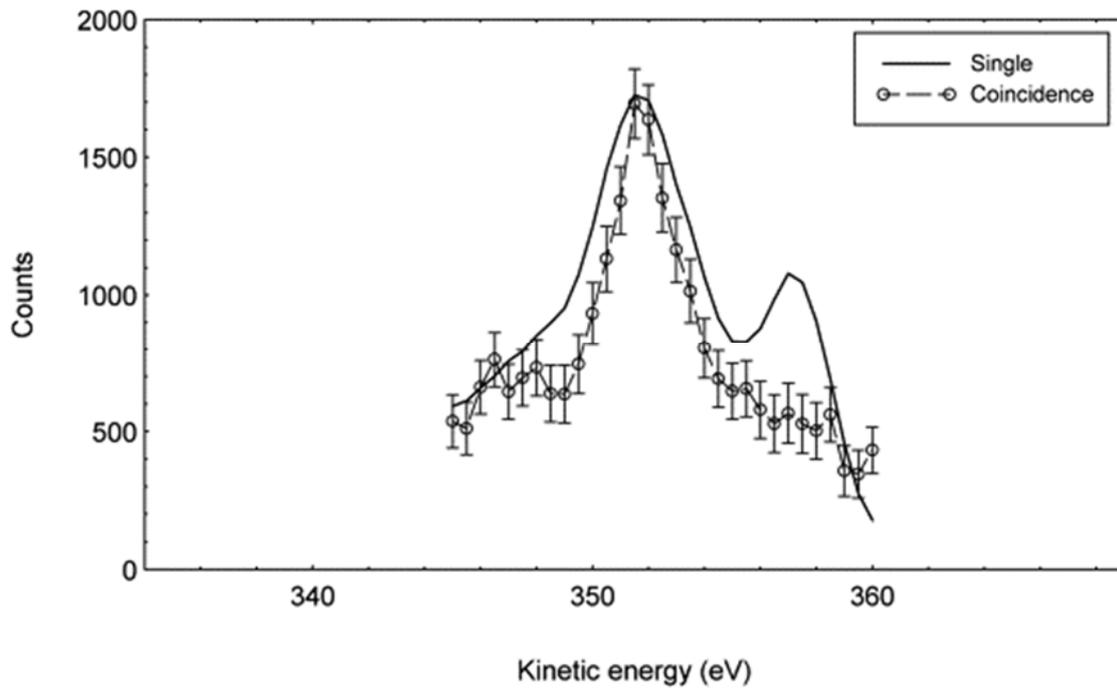
Fig. 5. The Ag $M_5N_{45}N_{45}$ Auger spectrum coincident with Ag $3d_{5/2}$(KE=886.0 eV) for $Ag_{0.5}Pd_{0.5}$ alloy. The solid line gives the regular single spectral data and the dashed line with error bar represents the coincidence data. The vertical dashed line is a reference line of Ag $M_5N_{45}N_{45}$ in $Ag_{0.5}Pd_{0.5}$ alloy.
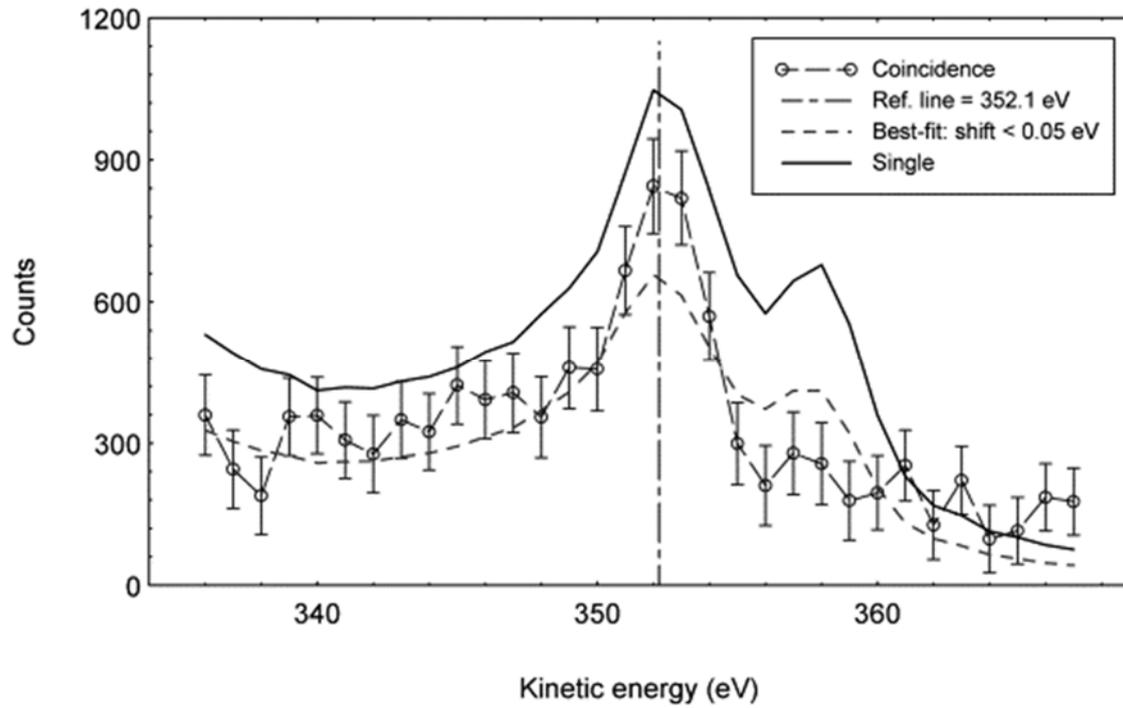
Fig. 6. Simplified model of the effect of varying the kinetic energy position of the analyzer used to detect the photoelectrons on the distribution of core electron energies sampled. The solid line and dashed line are approximations of the Ag $3d_{5/2}$ line measured in Ag and $Ag_{0.5}Pd_{0.5}$, respectively, using the Kratos-Axis Ultra instrument. The dotted lines represent the APECS apparatus analyzer response function at two different positions (±0.8 eV).
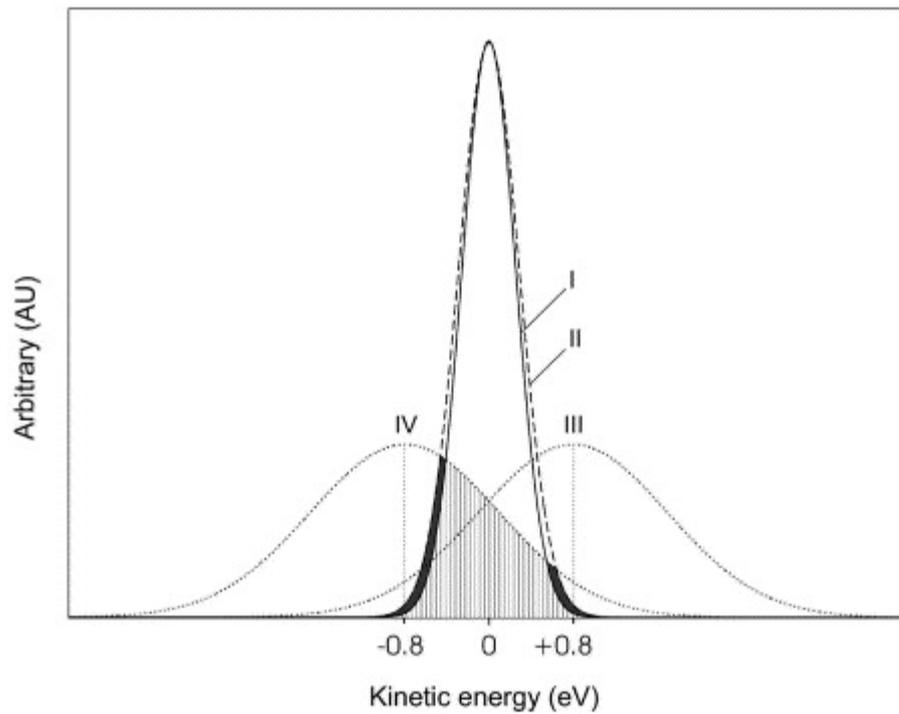
Fig. 7. The Ag $M_5N_{45}N_{45}$ Auger spectrum coincident with Ag $3d_{5/2}$(KE=886.8 eV) for $Ag_{0.5}Pd_{0.5}$ alloy. The solid line gives the regular single spectral data and the dashed line with error bar represents the coincidence data. The vertical dashed line is a reference line of Ag $M_5N_{45}N_{45}$ in $Ag_{0.5}Pd_{0.5}$ alloy.
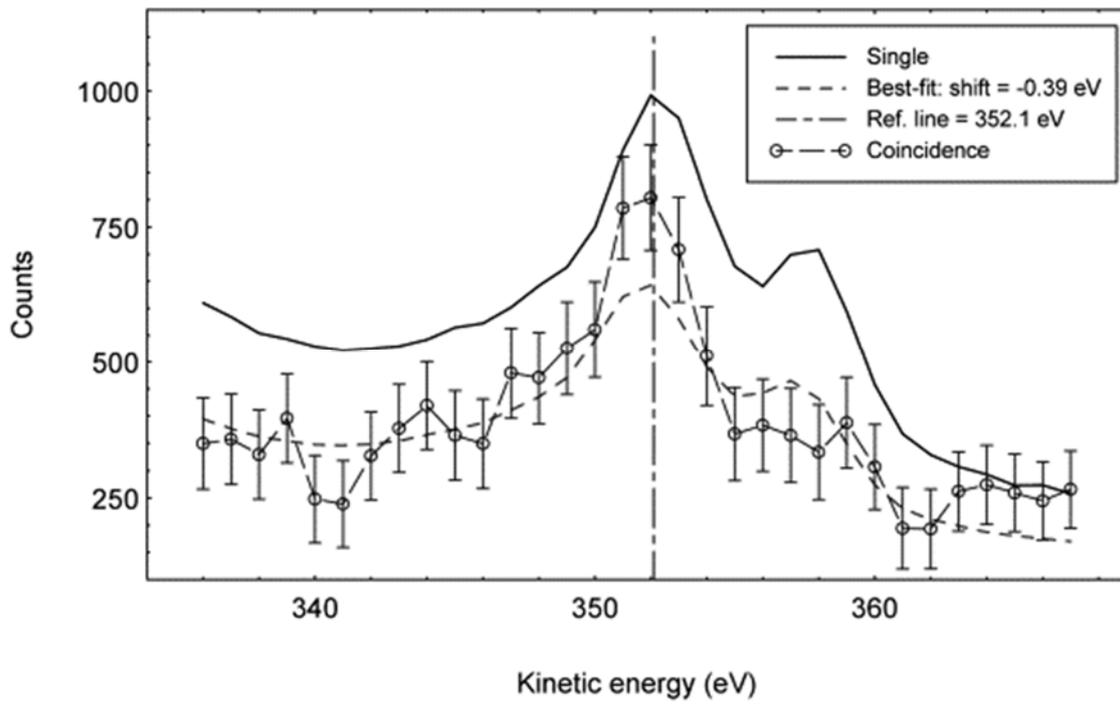
Fig. 8. The Ag $M_5N_{45}N_{45}$ Auger spectrum coincident with Ag $3d_{5/2}$(KE=885.2 eV) for $Ag_{0.5}Pd_{0.5}$ alloy. The solid line gives the regular single spectral data and the dashed line with error bar represents the coincidence data. The vertical dashed line is a reference line of Ag $M_5N_{45}N_{45}$ in pure $Ag_{0.5}Pd_{0.5}$ alloy.
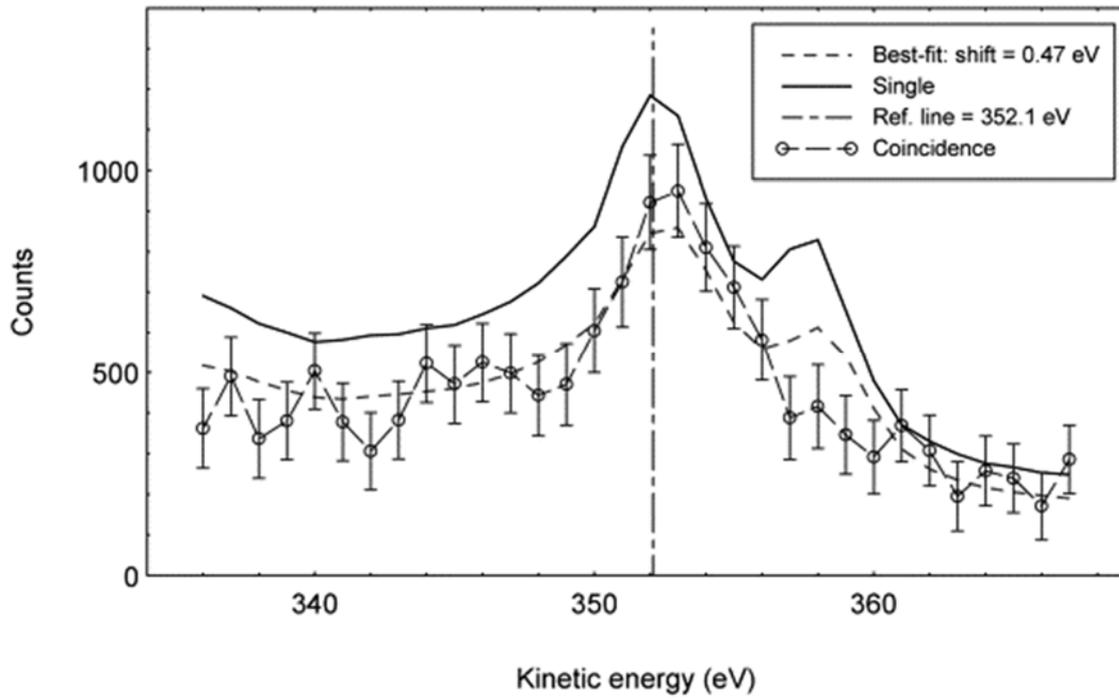
Table 1. A summary of XPS and AES lines for Ag, $Ag_{50}Pd_{50}$ and Pd. All photoelectron energies are shown as binding energy (in eV) while all Auger energies are shown as kinetic energy (in eV)

	Ag	$Ag_{50}Pd_{50}$	Pd
Agd $3d_{5/2}$ (BE)	368.14	367.58	
Ag $3p_{3/2}$ (BE)	573.18	572.56	
Pd $3d_{5/2}$ (BE)		334.72	335.65
Pd $3p_{3/2}$ (BE)		532.02	532.34
Ag $M_5N_{45}N_{45}$ (KE)	351.83	352.11	
Ag $3d_{5/2}$/eV (FWHM; Kratos)	0.59	0.68	
Ag $3d_{5/2}$/eV (FWHM; APECS)	1.92	2.15	
Ag $M_5N_{45}N_{45}$/eV (FWHM; Kratos)	3.26	3.54	
Ag $M_5N_{45}N_{45}$/eV (FWHM; APECS)	4.32	4.73	