Intrinsic Excitations in Deep Core Auger and Photoelectron Spectra of Ge and Si

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Photon induced transitions involving deep levels in the core of atoms in solids of great practical importance are gaining an increasing significance in quantitative analysis at buried interfaces or in determining local electronic structures in the bulk. An important issue of such applications of high-resolution, high-energy photon induced electron spectroscopy is the separation of the intrinsic spectral contributions (due to core hole creation, representing an inherent part of the photopeak) from those attributable to electron transport (extrinsic contributions).

In the present work, deep core Auger (Ge KLL) and Ge, Si photoelectron spectra excited by various energy X-rays are reported. A significant (30-60 %) contribution of intrinsic plasmon excitation to the spectra, depending on photon energy and core hole, has been observed, in a reasonable agreement with the dielectric theory.

INTRODUCTION

Photoinduced transitions involving deep atomic core levels in solid materials of great practical importance are gaining an increasing significance from the point of view of quantitative applications of electron spectroscopies. This relates e.g. to chemical state resolved concentration depth profiles of components at buried interfaces or the determination of electronic structures surrounding the initial state core holes in the bulk and interface regions of these systems. A better understanding of the response of semiconductor detectors to X-rays can be achieved, for instance, by the help of the knowledge of the core Auger spectra of the detector material. An important issue, seriously influencing the accuracy of the quantitative applications of high-energy resolution, deep core (up to 10 keV energy) photon induced electron spectroscopy is the separation of the spectral features attributable to intrinsic and extrinsic processes. The former relate to the core hole creation and represent a chemical state dependent inherent part of the photoinduced peaks while the latter appear as a consequence of the transport of the photo- or Auger electrons towards the solid surface. The detailed analysis of deep core photoelectron and KLL Auger spectra of Ge and Si shows strong intrinsic contributions to the intense satellite structures of the spectra - often explained only by electron transport processes. The comparison of the experimentally derived intensity share of the intrinsic and extrinsic contributions in the spectra to those calculated by models indicates the limits of validity of these models, facilitating the prediction of the magnitude and shape of the part of the spectra originated from intrinsic excitations.

In the present work, the results of studies on deep core Auger (Ge KLL) and Ge, Si photoelectron spectra, excited by various energy X-rays (characteristic and bremsstrahlung [1], tunable synchrotron radiation [2]) are reported, together with their interpretation using different models. A significant contribution of intrinsic excitation to the spectra, increasing with energy, has been observed, in a reasonable agreement with the dielectric theory [3].

EXCITATION OF PLASMONS IN PHOTO- AND AUGER EMISSION FROM SOLIDS

In photo- and Auger electron spectra from solids, distinct satellite structure due to plasmon excitation may occur [5]. A plasma oscillation in a metal (or doped semiconductor) is a collective longitudinal excitation of the conduction (free) electron gas and a *plasmon* is a quantum of a plasma oscillation [4].

Intrinsic plasmons *(created by the appearance of the core hole) [5]*

Assuming a free electron gas, the plasma frequency ω_p is given by $\omega_p = (4\pi \boldsymbol{n} e^2/m_e)^{1/2}$, where $\boldsymbol{n}$ is the density of the electron gas, e is the charge and m_e is the mass of the electrons. The dielectric function of the free electron gas (q=0) at frequency ω is expressed as:

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma_p \omega} \tag{1}$$

where $2\gamma_p$ denotes the full width at half maximum (FWHM) of the plasma resonance.

The energy loss function can be derived as (for small γ_p values):

$$\mathrm{Im}\left\{-\frac{1}{\varepsilon(\omega)}\right\} = \frac{1}{2}\frac{\omega^2}{\omega_p}\frac{\gamma_p}{(\omega-\omega_p)^2+\gamma_p^2} \tag{2}$$

The intrinsic plasmon spectrum consists of a serie of plasmon peaks positioned at energies $E_n = \hbar\omega_n$ and having FWHMs $\Gamma_n = 2\gamma_p$, with $\omega_n = \omega_0 - n\omega_p$ where n is the order of plasmons and $\gamma_n = \gamma_0 + n\gamma_p$ where γ_0 is the half of the FWHM of the photo- or Auger peak accompanied by the plasmon satellites.

The intensity distribution of the intrinsic plasmon peaks I_n is expected to follow a Poisson distribution:

$$I_n \propto e^{-b}\frac{b^n}{n!} \tag{3}$$

$$b = \left(e^2 c_q^2\right)/V_F \tag{4}$$

where c_q is the effective charge of the photohole seen by the conductive electrons and V_F is the Fermi velocity.

Extrinsic plasmons *(created during electron transport) [5]*

The intensity of the extrinsic plasmon peaks I_n is decreasing exponentially and can be approximated by $I_n \propto a^n$ where $a = \frac{\lambda_{tot}}{\lambda_{EP}}$ and λ_{tot} is the total mean free path of an electron with $\hbar\omega$ energy while λ_{EP} is the mean free path due to extrinsic plasmon creation

$$\lambda_{EP} = 4a_0\left(\frac{\omega}{\omega_p}\right)/\ln(\omega/E_F) \tag{5}$$

where a_0 is the first Bohr radius. The normalized intensity of the nth plasmon peak can be given by

$$\frac{I_p(n)}{I_0} = \left(b^n/n!\right) + a\frac{I_p(n-1)}{I_0} \tag{6}$$

Surface plasmons are collective excitations in the electron gas, similar to the bulk plasmons, which are, however, restricted in their spatial extension to the last atomic layer of the surface. The respective plasma frequency is

$$\omega_p^s = \frac{\omega_p}{\sqrt{2}}. \tag{7}$$

THEORETICAL MODELS DESCRIBING ELECTRON ENERGY LOSS IN SOLIDS

Quantum mechanical models

The extended QM model of Hedin [6] is based on a quasiboson model treating electron-boson coupling by fluctuation potentials related to the dielectric response function and connecting the dynamically screened potential in the bulk solid to the loss function. The model accounts for surface, extrinsic/intrinsic losses and interferences between them. Hedin's theory treats transition regime between sudden and adiabatic approximations and for semiconductors predicts a slow (keV) scale approach of the sudden limit as a consequence of strong destructive interference between extrinsic and intrinsic channels for plasmon production.

A formal theory for electron scattering and photoionization has been developed by Fujikawa [7], including the many-body theory of core-level photoemission by Keldysh Green's functions [8]. Fujikawa's theory describes intrinsic/extrinsic losses both for surface and bulk plasmons in XPS spectra excited from deep core levels. It treats effects of X-ray polarization, angular distributions for electrons emitted from the core levels of atoms at various depths, accounting for elastic scattering as well, X-ray Photoelectron Diffraction and resonances. The model predicts strong interference between extrinsic/intrinsic channels for any polarization at low photon energies.

Dielectric model for electron transport including core hole and surface effects

The quantum mechanical models mentioned above can give a quite detailed and coherent picture of the electron energy loss processes and are suitable for quantitative estimations, however, usually it is difficult to apply them generally to practically important cases.

The semiempirical dielectric model developed by Yubero and Tougaard [9] is proved to give a good agreement with experiment in a number of cases. This model assumes a semi-infinite medium ($\varepsilon(k,\omega)$) + a vacuum region ($\varepsilon = 1$) using pseudomedia for calculations. The electron-hole pair creation is described supposing a constant electron velocity and a stationary hole (small electron energy loss compared to the energy of the photopeak). It calculates the induced charge density during photoexcitation and electron transport and the energy loss caused by the induced electric field acting on the moving electron. For the total photoemission process the energy loss distribution is given in terms of the effective cross section for inelastic scattering (K_{eff}) which depends on the induced potential, the electron energy, the depth of electron-hole creation, the lost energy and emission angle [9]. The simulation of the experimental spectrum is performed by integrating K_{eff} over the electron path lengths (K_{sc}). $K_{eff} = K_{eff}$ (hole) + K_{eff} (electron), where K_{eff} (hole) describes the intrinsic, K_{eff} (electron) the extrinsic losses, their attenuation at integration over path length is different [9]. The simulated spectrum $J(E)$ describes only the first inelastic event [9]:

$$J(E) \propto \cos(\theta)\left[F(E) + \int_E^{\infty} dE' F(E')\lambda K_{SC}(E_0, E'-E, \theta)\right] \quad (8)$$

where $F(E)$ is the primary excitation spectrum (Lorentzian), K_{sc} the path integrated K_{eff}, θ the angle of emission; E the electron energy (E_0 the primary energy) and λ the inelastic mean free path of the electrons in the material.

PLASMON STRUCTURES IN PHOTOEXCITED ELECTRON SPECTRA OF SOLID Ge AND Si

Experimental

Ge layers of approx. 100 nm thickness were vacuum evaporated onto Si wafer substrates using a d.c. magnetron and cleaned in situ by Ar ion sputtering prior to the measurement. The Si data were obtained from a (100) single crystal wafer, in situ cleaned using standard procedures until a sharp (2x1) LEED pattern was observed.

Ge and Si 1s photoelectron spectra were excited and measured using the Tunable High Energy XPS facility at the BW2 beamline of HASYLAB/DESY (Hamburg) [10]. The photon energies applied for excitation were : 11.75 keV (Ge 1s); 3, 4, 5 keV (Si 1s), while the angles related to the surface normal of the samples were 45º for the incident photon beam (Ge and Si 1s) and 0º for the detected electrons. Ge $KL_{23}L_{23}$ Auger spectra were induced by Cu bremsstrahlung and measured with an energy resolution of 2.6 eV (at 8.5 keV), Si 2s, 2p photoelectron spectra were excited by Al Kα X-rays and measured using the ESA-31 spectrometer of ATOMKI (Debrecen) [11]. The related REELS measurements were performed using the ESA-31 spectrometer with an incident angle of 50º for the primary electron beam (having an energy set to correspond to the energy of the respective photoinduced peak) and with a detection angle of 0° for the emitted electron beam, related to the surface normal of the sample.

Evaluating the measured spectra, first REELS cross sections for inelastic electron scattering were obtained from the measured REELS spectra using Tougaard's method [12]. Inelastic background correction (removal of the contribution from extrinsic plasmon losses) of the measured photoinduced spectra

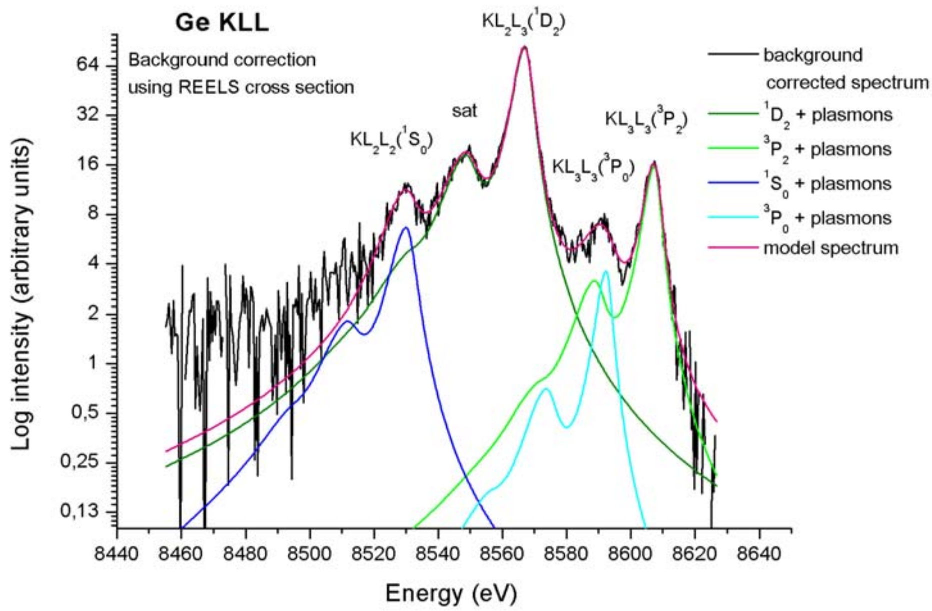

Fig. 1. The decomposition of the experimental Ge $KL_{23}L_{23}$ spectrum photoexcited from a polycrystalline Ge layer of 100 nm thickness.

was performed by deconvolution of the REELS inelastic cross section. In the case of the Si photoelectron spectra the 3 parameters universal cross section [13] was used. The share of the intrinsic energy loss contribution (from electrons suffered energy loss due to the appearance of a core hole) to the spectra was determined from the ratio of the intensity of the intrinsic plasmon peak (obtained from the spectra corrected for inelastic background) and of the intensity of the full plasmon peak derived from the measured spectra.

Spectra and interpretation

Ge KLL

The plasmon satellite structure near the KL_2L_3 ($^1D_2$) peak in the Auger spectra photoexcited from polycrystalline Ge was studied both experimentally and by model calculations [14]. The spectral shape could be described reasonably using the model spectra derived from the theory of Yubero and Tougaard [9] for energy loss processes in XPS. From the analysis of the measured and model spectra the share of the intrinsic plasmon excitation process is estimated to be between 30 and 40 % [14]. While the Yubero-Tougaard model accounts for the first intrinsic plasmon excitation, the analysis of the whole $KL_{23}L_{23}$ spectral region shows [15] that a consistency with the atomic calculations and with the spectra emitted from extremely thin radioactive samples can be achieved only by taking into account the presence of the second intrinsic plasmon as well and assuming the Poisson distribution for the intrinsic plasmon intensities as mentioned above. Figure. 1 shows the decomposition of our experimental Ge $KL_{23}L_{23}$ spectrum (corrected for inelastic background using REELS cross section) photoexcited from a polycrystalline Ge layer of 100 nm thickness.

Si 1s

Si 1s photoelectron spectra (normalized at their peak maxima) excited from a single crystal sample using 3, 4, and 5 keV energy monochromatized photons, can be seen in Fig. 2. The intensity of the plasmon peaks increases with the photon energy. Following correction of the spectra for inelastic background using the 3 parameters universal cross section and Tougaard's method, this tendency remains similar. The corrected spectra were fitted

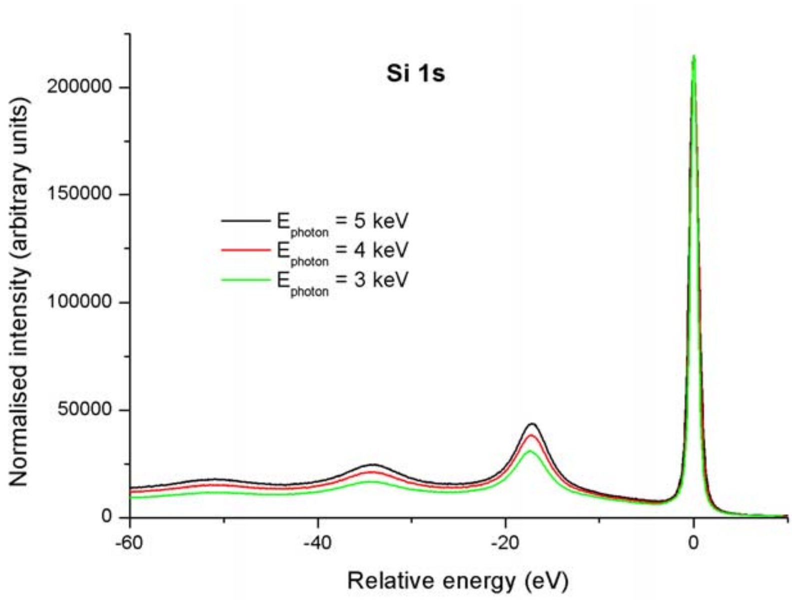

Fig. 2. Normalized Si 1s photoelectron spectra excited from a Si single crystal sample by monochromatized X-ray photons of 3, 4, and 5 keV, respectively.

with asymmetric Lorentzians assuming the Poisson distribution for describing the intensities of the intrinsic plasmon peaks. The estimated share of intrinsic plasmon excitation is ca 38, 46 and 51 % for the exciting photon energies 3, 4 and 5 keV, respectively, clearly increasing with photon energy, in agreement with the dielectric theory [16]. The value of the *b* parameter of the Poisson distribution (ca 0.35) is practically independent of photon energy.

Si 2s, 2p

Figure 3 shows the decomposition of the Si 2s, 2p photoelectron spectrum excited by Al Kα X-rays from an amorphized single crystal sample. The photopeaks were fitted by Doniach-Sunjic type asymmetric lineshapes completed by an intrinsic plasmon series tail attenuated according to the Poisson distribution. The component representing the Tougaard-type inelastic background, based on the 3 parameters cross section, is also indicated. As it can be seen in the Figure, this model describes the measured spectrum quite well. For the parameter *b* a value of 0.26 is obtained, while the estimated share of the intrinsic plasmon excitation is approximately 50 % (Si 2p) and 58 % (Si 2s).

SUMMARY

Ge KLL, Si 1s (at exciting photon energies of 3, 4 and 5 keV) and Si 2s, 2p spectra photoinduced from pure solids were measured and analyzed to obtain information on the share of intrinsic processes in plasmon excitation. The results show a significant (30-60 %) contribution of intrinsic plasmons to the spectra, depending on core hole and photon energy, in agreement with the prediction of the dielectric theory. Simple methods are proposed for accounting intrinsic plasmon excitation in Ge and Si in quantitative analytical applications of high energy electron spectroscopies.

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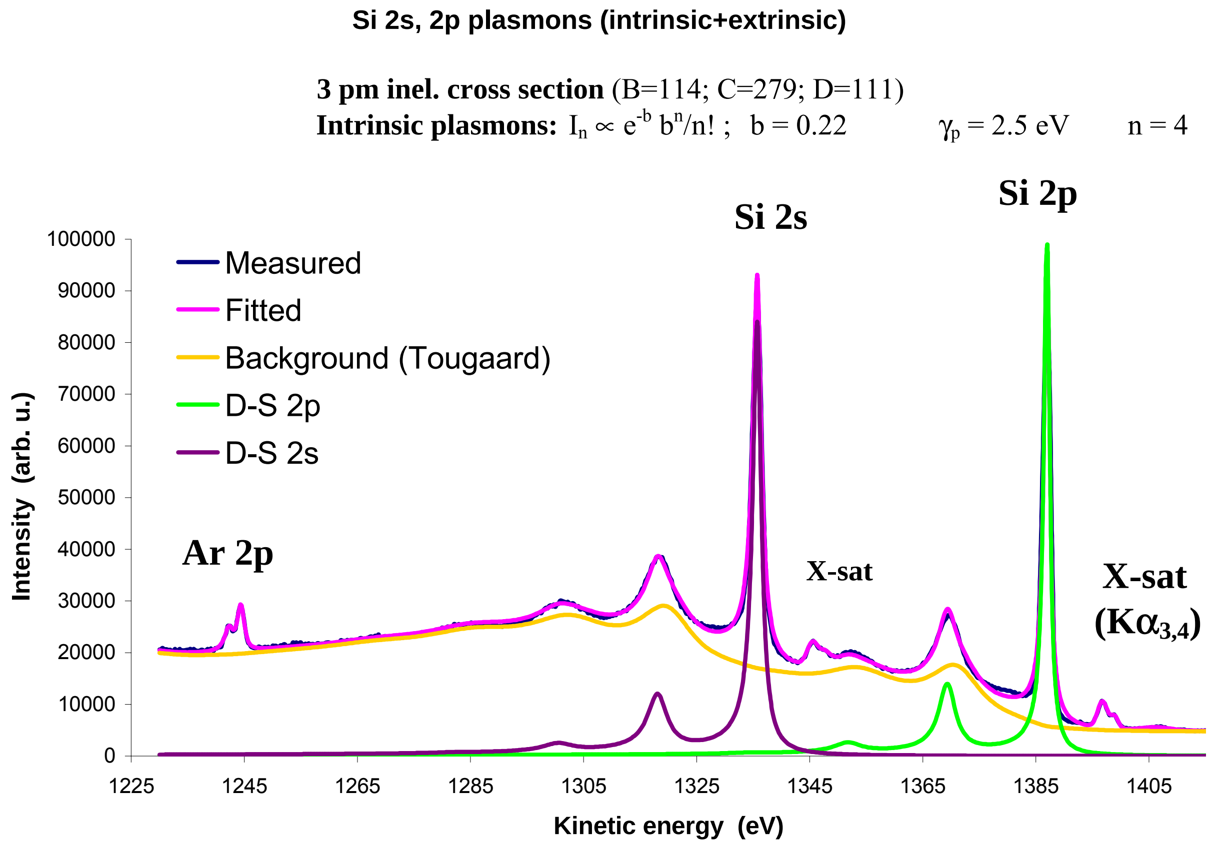

Fig. 3. The decomposition of the Si 2s, 2p photoelectron spectrum excited by Al Kα X-rays from an amorphised single crystal sample.

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