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To cite this version:
M. Brunel, B. Gilles. GRAZING INCIDENCE X-RAY FLUORESCENCE. Journal de Physique Colloques, 1989, 50 (C7), pp.C7-85-C7-96. <10.1051/jphyscol:1989708>. <jpa-00229681>

HAL Id: jpa-00229681
https://hal.archives-ouvertes.fr/jpa-00229681
Submitted on 1 Jan 1989

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GRAZING INCIDENCE X-RAY FLUORESCENCE

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RÉSUMÉ : Un faisceau de rayons X (λ=1 Å) arrivant sur une surface à une incidence α de 1 ou 2/10° de degré est totalement réfléchi et l'onde transmise dans le matériau est évanescente. La fluorescence, si elle est excitée, dépend de la composition chimique d'une couche de 20 à 30 Å c'est à dire de quelques monocouches. La sensibilité aux impuretés de surface est alors exceptionnelle (10¹¹ at/cm²). Quand on accroit l'angle α, la profondeur irradiée varie de quelques dizaines d' Å à plusieurs µm et la variation If(α) de l'intensité de fluorescence est reliée au profil de concentration par une transformation de Laplace. Les applications sont multiples : profils de densité, de composition, d'implantation. Des profils structuraux ou d'amorphisation peuvent être obtenus par la même méthode, en observant les variations d'intensité de diffraction. La fluorescence en emergence rasante permet de déterminer un profil d'état chimique.

Abstract : An X-ray beam (λ=1 Å) falling on a surface at an incidence angle α of some tenths of a degree is totally reflected and the wave transmitted into the material is evanescent and is rapidly absorbed. If excited, the fluorescence depends on the chemical composition of the 20 or 30 Å irradiated layer near the surface. The sensitivity to the impurities at the surface is exceptional (10¹¹ at/cm²). When the angle α increases, the irradiated depth changes from several tens of angstroms to several µm and the variation If(α) of the fluorescence intensity is related to the concentration depth profile through a Laplace transform. This technique is applied to the density, composition and implantation profiles. Structural and amorphous profiles can be obtained from the change of the diffracted intensity with α. One can also use grazing exit fluorescence : in this case, the sample is irradiated at normal incidence and the X-ray emission is observed at grazing emergence. A chemical state profile can be determined by comparing the variations of the emission spectra with α.

INTRODUCTION

X ray beams with wavelength around 1 Å do not seem to be convenient tool for the study of surfaces and thin layers because their attenuation length is on the order of ten µm (70 µm for λCuKα in silicon). If the incident angle α between the
beam and the surface is reduced to some 1/10th of a degree, the propagation of
the transmitted wave in the material becomes evanescent. Its depth of
penetration \( \tau \) (1 measured at \( i/e \) of the intensity) is on the order of 20 to 50 Å.
In this case, fluorescence and diffraction depends on the atomic arrangement and
chemical composition of some monolayers. If we increase the incident angle of
the beam on the surface, the depth \( \tau \) increases. This provides a probe for the
investigation of changes from the surface of the material to a depth of some tens
of \( \mu \)m.

Here, we will only consider the fluorescence, in grazing incidence and we will
show that this technique is very sensitive to surface impurities and that a
chemical depth profile can also be determined. These results are comparable with
those obtained by methods such as SIMS or RBS. The grazing exit angle method
can also give interesting information on the chemical state of the atoms at or near
the surface.

Finally, we will apply the above methods, used for depth profiling, to study
diffraction and diffusion with angular variation.

I ) PROPAGATION OF WAVES

An electromagnetic plane wave is incident at a grazing angle to the surface of a
homogeneous material, with refractive index \( n \). The angle between the direction
of the wave and the surface is \( \alpha \). For an X-ray wave (\( \lambda = 1 \AA \)), \( n=1+n'+in'' \), with \( n' \)
and \( n''<0 \) of the order of \( 10^{-6} \).

Fresnel's laws \cite{1} show that

1) when \( \alpha \leq \alpha_c = \sqrt{-2n'} \), the Descarte's law, \( \sin i=n \sin r \), has no real solution and a
reflected wave appears whose intensity is almost equal to that of the incident
beam. This intensity decreases sharply near the angle \( \alpha_c \).
2) the electric field vector of the transmitted wave is of the form

\[
\mathbf{E}(x, z) = A(\alpha) \exp(-z/2\tau) \exp \{ i\omega t - \frac{2\pi}{\lambda} (x \cos \alpha + z R(\alpha)) \} \quad (1).
\]

\( x \) is parallel to the surface and \( z \) is perpendicular to this surface.

The factor \( \exp(-z/2\tau) \) is characteristic of an evanescent wave, with an amplitude
\( A(\alpha) \) and a penetration depth \( \tau(\alpha) \).

If \( R(\alpha) \) and \( J(\alpha) \) are the real and imaginary parts of \( \sqrt{\alpha^2+2n'+2in''} \) \cite{2}, then:

\[
A(\alpha) = 2\alpha/\sqrt{(R(\alpha)+\alpha)^2 + J^2(\alpha)} \quad \text{and} \quad \tau(\alpha)=\lambda/4\pi J(\alpha)
\]
The refractive index $n$ is related to the electronic density of the material and to its linear absorption coefficient $\mu$ [3] by

$$n' = (-e^2/mc^2) \lambda^2 N(Z + f')/2\pi$$

$$n'' = (-e^2/mc^2) \lambda^2 Nf''/2\pi = (\lambda/4\pi)\mu$$

$f'$ and $f''$ are the real and imaginary dispersive corrections respectively, and $e^2/mc^2=2.82\times10^{-13}$ cm.

For the CuKα=1.54Å radiation, $\alpha_c$ ranges from 0.2° to 0.6°. The penetration depths calculated for some materials are reported in fig (1).

![Graph showing depth of penetration](image)

**Fig 1: Depth of penetration $\tau(\alpha)$ into B, Si and Ti samples at $\lambda$CuKα**

The validity of this calculation is demonstrated by the good agreement with the experimental penetration depth $\tau_{Si}(\alpha)$ in silicon determined by the broadening of the Bragg peaks. Note that $\tau(\alpha)$ decreases rapidly at $\alpha=\alpha_c$: it reaches low $\alpha$ angle values of 20 to 50 Å relatively independent from the density and nature of the material, and also from the incidence angle $\alpha$.

The application of this method is straightforward: if we are interested in the scattering of a small plate or of a thin layer near its surface, the observation at grazing incidence will strongly reduce the background scattering of the substrate. As a matter of fact, a change in $\alpha$ by a factor of 100 between 15° and 0.15°, involves a decrease from 18 μm to 45 Å (factor of 4000) in the penetration depth ($\lambda$CuKα).
The use of the grazing incidence technique may be limited by the roughness and the sample curvature. We shall not address these problems here; they are treated by Nevot and Croce [4], for reflected beams, and by Robinson for diffraction. It seems that, in general, optical polishing is sufficient for grazing incidence X-ray study.

II) ANALYSIS BY GRAZING INCIDENCE X-RAY FLUORESCENCE

If the energy of the incident beam is strong enough, the transmitted wave will excite the fluorescence of the atoms in the irradiated layer, that is to say some tens of Å.

The experimental setting is very simple (fig 2) and can be the same for fluorescence and diffraction, except for the movement of the detector. The X-ray beam, preferentially monochromatic, is issued from a classical tube (1500 w) or from a rotating anode tube. It is limited by some slits and is incident on the sample at a very low angle. The solid state detector (SiLi with window of 80 mm²) that is set in front of and very near to the sample, collects the emitted X-ray photons. The signal is recorded in a multichannel analyser. The analysed surface can be reduced to some mm² by slits between the sample and the detector window.

![Diagram of experimental setup](image)

**Fig 2 : Experimental set-up**

For light elements (low z), or for reducing the background scattering, the sample is set in a vacuum and the window of the detector taken off. In favorable cases, impurities such as transition metal atoms (Cr, Fe, Ni,..) or W, Au... at the surface of a light substrate such as silicon, can be detected with a sensitivity of some $10^{11}$ at/cm² to $10^{12}$ at/cm² (1/10000 to 1/1000 of a monolayer!).

Therefore, we can measure the impurities, Iron in particular, deposited during the plasma etching on the surface of the silicon wafers. The impurity rates, determined quantitatively by a comparison with the fluorescence of an implanted sample ($10^{15}$ iron implanted in silicon), vary from $10^{12}$ to $10^{14}$ iron atoms/cm².
(fig 3) according to the conditions of the plasma etching (type of the reactor, tension,...). These metallic impurities may imply detrimental effects on performance and yield of integrated circuits.

![Graph showing fluorescence from iron and nickel impurities on a silicon wafer after plasma etching.](image)

**Fig 3**: Fluorescence from iron \((2 \times 10^{13} \text{ at/cm}^2)\) and nickel \((4 \times 10^{13} \text{ at/cm}^2)\) impurities on a silicon wafer (after plasma etching): incident beam \((\lambda \text{CuK}\beta\text{)}, \text{in air}\).

This technique named TXRF (Total Reflection X-ray Fluorescence) is in competition, or in complementarity, with "heavy" techniques like SIMS or RBS and has been used recently in microelectronics laboratories and production to detect and measure the contamination rate due to the polishing, the plasma processes, the oxidation, and the ion implantation on the silicon wafers.

Beside its simplicity, the x-ray fluorescence has some other advantages. It does not damage the sample, which may be studied after different treatments and does not require any sample preparation. Eventually, X Ray fluorescence does not take a long time (some minutes). However, the lateral resolution is only some mm².

**III) OBSERVATION WITH VARIABLE INCIDENCE**

We have seen that the depth of penetration of the transmitted beam can be changed by varying the angle of incidence around \(\alpha_c\).

If the chemical composition of the sample is homogenous with depth, the intensity of the beam at the depth \(z\) is:

\[
I(z, x) = I_{\text{incident}} \, A^2(\alpha) e^{-z/E(\alpha)}
\]

and the intensity of fluorescence \(I_F(\alpha)\) is:
The constant \( C \) takes into account the fluorescence cross section, the detector efficiency, etc...

\[ I_F(\alpha) = CN \int_0^\infty I(z,\alpha)dz = C \ln N A^2(\alpha) \tau(\alpha) \]

\( N \) is the number of excited atoms in a layer of unity thickness and surface equal to the surface of the solid seen from the detector.

\( A^2(\alpha) \) and \( \tau(\alpha) \) can be calculated by Fresnel relations and the variation of intensity as \( A^2(\alpha) \tau(\alpha) \) is observed experimentally [2][6] as shown in figure 4.

When the density of the material is unknown, it may be determined from the variation \( I_F(\alpha) \) of the fluorescence by measuring the critical angle \( \alpha_c \) or more accurately by fitting experimental and calculated curves. The same variation \( I(\alpha) \) in \( A^2(\alpha) \tau(\alpha) \) is expected for the integrated intensity of Bragg reflection, but dynamical effects disturb the function \( I(\alpha) \).

We used this technique to determine the density of porous silicon samples prepared in different conditions of doping and electrochemical etching. The densities obtained by X-ray fluorescence are in good agreement [7] with results derived from gravimetric measurements on thick layers (10 \( \mu \)m), but the X-ray method can be used on thin layers (some thousand of \( \AA \)). For some samples, the density is 30% of that of silicon, but the roughness due to the numerous cylindrical voids (\( \sim100\AA \) in diameter) does not significantly modify the curves \( I_F(\alpha) \) as can be seen in fig 4.

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Fig 4 : Variation \( I_F(\alpha) \) for silicon and two different porous silicon : \( P+25\%HF \) with \( d=0.63d \) (silicon) and \( P+10\%HF \) with \( d=0.33d \) (silicon). The lines are calculated curves.
For porous silicon, the more classical method of density determination, using X-ray reflected beam (determination of $\alpha_c$), gives a density which is too large (about 30%). This disagreement might be due to roughness effects which are more significant at angles $\alpha < \alpha_c$.

IV) IMPURITY PROFILE

If the concentration $C(z)$ of the impurity varies with the depth $z$, the change of intensity of the fluorescence with $\alpha$ is given by the integral of the product of the beam intensity (emission effects are incoherent), at the depth $z$, with the number of impurities at this depth [8]. This intensity is:

$$I(\alpha) = CA^2(\alpha) \int_0^\infty N C(z) \exp[-z/\tau(\alpha)]dz \ (3)$$

with $C$, $A^2(\alpha)$, $\tau(\alpha)$ and $N$ as defined previously.

This relation is valid only if the impurity is dilute enough so that it does not change the transmitted X-ray beam.

The application is interesting for impurities near the surface (<1 μm) and the limit of $I(\alpha)$ for great values of $\alpha$ ($\alpha = 1$ or 2°) is proportional to the total number of impurity.

According to (3), the experimental function $I(\alpha)/A^2(\alpha)$ is the Laplace transform of the concentration profile $C(z)$, thus $C(z)$ can be determined from $I(\alpha)$. In fact, we do not compute this Laplace transform directly because it is difficult to take into account some experimental parameters like the divergence of the beam and the angular shift. Instead, we used a method of approximation into stratified layers; so the modification of the beam by the impurities can be taken into account.

This method is general for all studies at grazing incidence (diffraction, reflection) and will be developed here.

The concentration profile $C(z)$, which is assumed to be known, can be approximated by steps with a constant concentration in each step. Then, the volume element contaminated by the impurity is substituted by a stack of strata parallel to the surface [9] [4]. The calculation of $I(\alpha)$ is replaced by the calculation of a wave propagating into a stratified medium.

When $\alpha < \alpha_c$, 4 waves interfere at each interface between strata (i-1 and i) (fig 5) except at the interface between the layer n and the substrate.
Fig 5: Waves in the stratified layers approximation

Their amplitudes $E$ are related by:

$$E_{U, i-1, b} = T_{i, i-1} E_{U, i, h} + R_{i-1, i} E_{D, i-1, b}$$

$$E_{D, i, h} = R_{i, i-1} E_{U, i, h} + T_{i-1, i} E_{D, i-1, b}$$

$$T_{i-1, i} = 2 R_{i-1, i} / (R_{i-1, i} + R_{i})$$

$$R_{i-1, i} = (R_{i-1, i} - R_{i}) / (R_{i-1, i} + R_{i})$$

$U$ and $D$ signify waves which go "up" and "down", and $h$ and $b$ signify the top and the bottom of the layer.

$R_{i, i-1}$ and $T_{i, i-1}$ are the coefficients of reflection and transmission at the interface $i-1$; $i$; both can be deduced from Fresnel equations. The interfacial planes are parallel to the surface. The direction of propagation and the attenuation of the waves into a layer depends only on the index $n$ of this layer and on $\alpha$.

$$\mathcal{R}_{i}(\alpha) = (\alpha^2 + 2 n_i^2 + 2 n_i^* n_i)^{1/2}$$

The boundary condition requires that only one wave can propagate down in the last layer which is the media without impurities. A recurrent calculation from the last bottom to the first top gives all the waves in the different layers. Because the fluorescence intensity is incoherent, the total intensity is only the sum of the integrals into each layer:

$$I(\alpha) = \sum_{i} N C_i \int_{z_i} |E_{D, i, b} \exp(-ik_i z) + E_{U, i, d} \exp(ik_i z)|^2 dz$$

with $k_i = 2 \pi \mathcal{R}_{i}(\alpha) / \lambda$.

With this relation one may calculate $I(\alpha)$ if $C(z)$ is known. In fact, $C(z)$ is not known and we used a fitting method which refines the parameters $C_i$ in order to minimize the function.
\[ F = \sum_{\alpha_1} \left| I_{\exp}(\alpha_i) - I_{\text{cal}, \text{ci}}(\alpha_i) \right|^2. \]

An interesting application is the determination of the implantation profile \( C(z) \) for the ions introduced into the material by implantation [10] [8]. The theoretical function is a gaussian but the experimental profile may be different.

Here, we give the example of iron implanted in silicon at different energies between 35 K\( \text{v} \) to 100 K\( \text{v} \). The amount of implanted ions varies from \( 10^{15} \) (= 1 monolayer) to \( 10^{16} \) at/cm\(^2\).

![Variations of \( R(\alpha) = I_{Fe}(\alpha)/I_{Si}(\alpha) \) for different implanted silicon samples.](image.png)

**Fig 6**: Variations of \( R(\alpha) = I_{Fe}(\alpha)/I_{Si}(\alpha) \) for different implanted silicon samples.

The experimental setting has been described previously, in this paper and we report in fig 6 the variations of \( R(\alpha) = I_{Fe}(\alpha)/I_{Si}(\alpha) \), in which \( I_{Fe}(\alpha) \) and \( I_{Si}(\alpha) \) are the intensities of K\( \alpha \) fluorescence for iron and silicon. The intensity is normalized at \( \alpha = 1 \), and we observe very different graphs according to the energy of implantation. The ions near the surface, which are more numerous at low energies (35Kv), are excited at low \( \alpha \) angles, by a totally evanescent wave and a high flux due to the refraction of the wave. This can be seen from the values of \( A_2(\alpha) : A_2(\alpha=0.22^\circ) = 3.35 \) and \( A_2(\alpha=0.35^\circ) = 1.25 \).

We have reported in fig 7 the profile \( C(z) \) obtained for the sample (35Kv-\( 10^{15} \) at/cm\(^2\)) in using the stratified media method. The profile \( C(z) \) at the beginning of the fit is only the function \( C(z) = \text{constant} \) for \( 0 \leq z \leq z_{\text{max}} \).
Fig 7: Implantation profile 10^15 at/cm² of iron implanted in silicon at 35 Kv.

The "fluorescence" profile is in good agreement with the profile determined by SIMS. This is also true for the position of the center of gravity (385 Å and 380 Å respectively) and for the quadratic width (195Å and 180 Å). The results of the two experimental methods disagree with the position (300 Å) and the width (120 Å) of the calculated Gaussian function.

The depth resolution, limited by the divergence of the fit when the layers are too thin, is of the order of 30 to 40 Å at the top of the material and 200 Å at 1000 Å depth. For SIMS, the resolution is, of the order of 50 Å and evidently depth independent.

The X-ray method can be used very easily in air, in vacuum or under controlled atmosphere and for liquid surfaces.

This possibility was used to determine the polymer concentration at the air liquid interface, for a polymere dissolved in a solvent. The comparison of the variation I_F(α), for the manganese atom attached to the polymer, and the variation I_F(α) for the sulfur atom of the solvent, measured with synchrotron radiation, shows a strong attraction of the polymer to the surface. This creates a rather dense layer, a couple of hundred Å thick, at the liquid air interface [10]. The same type of measurement was used recently on MnCl₂ dissolved in water and covered by a monolayer of stearic acid. The experimental I(α) fluorescence of Mn shows a dramatic segregation of the metal ion from the liquid bulk to the liquid/gas interface [12].
V GRAZING EXIT:

The principle of reversibility can easily explain the grazing exit: for a material irradiated at normal incidence, the fluorescence observed at grazing emergence is due to the emission of a thin layer near the surface. This fact was verified experimentally [6].

The emission spectra of one element depends on its chemical bonds. This chemical perturbation modifies the emission related to the valence shell-inner orbital transitions like Kβ lines.

It should be possible by the observation of the emission spectra at grazing exit angles, to deduce the chemical state of elements at the surface. If this observation is made by varying the exit angle around \( \alpha_c (\lambda_i) \), which is the critical angle of reflection for the wave emitted by element i, we can obtain a chemical profile by the method previously described.

The slight change in the emitted spectra due to chemical bonds requires that the resolution of the analyser must be on the order of a few eV. This implies the use of a monocrystal and a great loss of photons.

This type of experiment was performed with soft X-rays and at angles of \( \alpha > \alpha_c \) [12]. We have also undertaken a study of oxydized steel samples. Here the sample is irradiated at normal incidence with the white beam of a rotating anode tube. Use of a dispersive analyser and a position sensitive detector reduces the time of the experiment.

VI GENERAL USE OF THE METHOD OF VARIABLE INCIDENCE:

Impurity profiles are determined from the variation \( I_F(\alpha) \) of the intensity of fluorescence. In the same way, profiles of structural phases or crystalline state, can be obtained from the variations of the diffracted intensity with the incidence angle.

In Si, partially amorphised by ionic implantation of Si, the depth profile of the amorphous phase was deduced from the variation with \( \alpha \) of the diffused broad peaks characteristic of amorphous state [13]. At the same time, changes in the intensity of a Bragg peak give a profile of the crystallised phase complementary to the amorphous one. These profiles show an evidence of an undisturbed crystalline state at the surface.

CONCLUSION

For the characterisation of surfaces or thin layers, an old and simple method like X-ray fluorescence used at grazing angle is competitive with, and complementary to, heavy and complex techniques.

As with the SIMS method, fluorescence is sensitive to a sub monolayer surface contamination. At present, the fluorescence is used for the control of silicon wafers.
Density of homogeneous material can be determined. This application is interesting for porous materials and for non-continuous deposits, as we have shown in the case of deposited Si on Al₂O₃ [7].

Depth profiling of chemical composition is related to the variation \( I(\alpha) \) of the fluorescence of the elements. These profiles are usually obtained by SIMS, RBS or Auger methods.

Finally, the results that can be obtained by X-ray emission spectroscopy at grazing exit complement those gained from photo electron spectroscopy.

As said previously, the X-ray methods have the great advantage that they may be applied to solids and liquids as well, and work in atmosphere or in vacuum.

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