Characterization of Planarity of Polymer Thin Films on Rough Surfaces

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ABSTRACT

Angular dependent total reflection x-ray fluorescence (TRXF) is used to characterize the surface roughness or the extent of planarization of a thin polymer coating on a stainless steel surface with significant roughness. The objective of this work is to explore the use of TRXF as a non-contact and quantitative technique for characterizing surface roughness of thin film coatings. Once developed, this technique is expected to perform equally well on other surface coating materials other than polymers. Unlike optical methods, whether the thin films are transparent or not is not expected to affect the outcome of this measurement. TRXF data were collected with incident angle in the region around the polymer critical angle and were analyzed in conjunction with the results deduced from specular x-ray reflectivity (XR). Comparison between the TRXF results and those obtained from atomic force microscope (AFM) was also made in order to evaluate this TRXF method critically.

1. INTRODUCTION

The smoothness or planarity of thin film coatings is of central importance to many aspects of modern electronics. In building up a multilayer chip the surface smoothness of each interlevel dielectric layer is a main concern, and quite often chemical mechanical polishing is needed to planarize each dielectric layer. A typical thickness for interlevel dielectrics is about one micrometer. In this thickness range most of the current dielectric materials, e.g. CVD silica, polymers, spin-on glass, are transparent to light in the visible wavelength range. This is an intrinsic difficulty of any optical detection methods when applying on thin transparent coatings. To circumvent this difficulty we chose x-ray as the probe and the purpose of this work is to explore the angle-dependent total-reflection x-ray fluorescence (TRXF) for the surface characterization of thin coatings.

The effect of surface roughness on angle-dependent total-reflection x-ray fluorescence has been considered both experimentally [1, 2] and theoretically [3] for the fluorescent species directly resident on the rough surface. The case of a thin film with a given surface roughness on top of a substrate made up of the fluorescent element has been recently explored by the present authors [4]. This situation is shown in Figure 1. The angle-dependent total-reflection x-ray fluorescence in this case should be a sensitive measure of thin-film roughness and is a novel way to characterize rapidly the planarity of thin films. This could be especially useful for studying dielectric planarization over metal topography in microelectronics applications.

At the x-ray wavelength of a few Angstroms the refractive index of material is less than unity, hence, there exists a critical angle below which total internal reflection takes place. For a smooth thin-film coating, analyzed by means of a well-collimated incident x-ray beam, the fluorescence intensity is zero if the x-ray penetration depth is less than the film thickness. At a grazing incident angle below the critical angle for total reflection, the penetration depth is typically limited to a few nanometers depending on the x-ray index of refraction of the thin-film material. In this case only a negligible fluorescence signal can be measured for films thicker than the evanescent wave penetration depth, typically 10 nm depending on beam divergence and other factors. At the critical angle and above, the penetration depth goes to infinity (absent effects of x-ray absorption) leading to a steep rise in fluorescence. Such a sharp transition

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of the substrate fluorescence intensity near the coating critical angle gets smoothed out if the thin-film surface is rough. This is because on a rough surface the local incident angle can vary significantly from the macroscopic incident angle. A well defined transition between the absence of a fluorescence signal and the presence of a fluorescence signal at the critical angle can disappear completely for very rough surfaces.

Theoretically, x-ray reflectivity results including both specular and off-specular components, contain all the surface topology information. The analysis of off-specular data is in its developing stage, and the analysis of specular data has been conducted in a highly simplified way. It has been treated as a one-dimensional problem and the off-specular events are completely excluded in such a treatment. Within the context of current XR data reduction schemes surface roughness is simply modeled as a density gradient while any lateral fluctuations or true roughness are completely ignored. Even a density gradient can enhance the penetration depth of the incoming x-ray, hence the fluorescence from the substrate, just as surface roughness does, XR is not expected to be a sensitive tool for surface topology. Another objective of this work is to demonstrate that angle-dependent TXRF can provide roughness information that is quite different from that provided by (XR). More specifically we are going to demonstrate that TRXF can not be modeled or predicted based on XR results alone, i.e. surface gradient is not a substitute for surface roughness and XR can not substitute for TRXF.

2. EXPERIMENTAL

A highly polished stainless steel disk of 10 cm diameter and 1 cm thick was used as the substrate. Based on an optical interferometer measurement its surface flatness is within 150 nm across the whole surface. Polymer thin films with controlled surface roughness were prepared using a phase-separated blend of polystyrene and poly (vinyl methyl ether) (PS/PVME) . The PS/PVME blend thin films were prepared by spin coating from a 2% wt. solution. The polystyrene for the blend work had a relative molecular mass of 220,000 g/mol and a polydispersity of 1.02. The PVME was synthesized via anionic polymerization and had a relative molecular mass of 345,000 g/mol and a polydispersity of 1.45. A molar ratio of 3/7 was used to make the PS/PVME blend. This blend is rather unstable in thin film form [5], consequently phase separation proceeds readily upon heating. The blends were annealed at 150°C in air for various times to create thin-film surfaces with varying degrees of roughness.

The specular reflectivity and the angle-dependent TRXF measurements were conducted in a theta-2theta configuration with a copper x-ray tube. The incident beam was conditioned with a four-bounce Germanium [220] monochromator. Before the detector the beam was further conditioned by a three-bounce Germanium [220] channel cut crystal. This setting results in a copper $K_{\alpha 1}$ beam with a wavelength spread of 1.3×10^{-4} and a angular divergence of 12 arcseconds. The motion of the goniometer is controlled by a close loop servo system with a angular precision and reproducibility of 0.0001°. The fluorescence was measured with a energy-dispersive detector placed directly above the illuminated area at a distance of 5 mm. The energy window was set at 6.40 keV, that of the iron K_{α} line form the stainless steel substrate and had a window width of 510 eV. TRXF measurements were conducted on the bare stainless steel surface as well as surfaces coated with PS/PVME films after different annealing times.

All the sample surfaces were also examined using an atomic force microscope (AFM). It was operated in a non-contact mode with a scanning speed of 100 μm/s over an area of 100 μm x 100 μm . Rescan of the same area revealed no difference in image indicating that this scanning scheme did not introduce any measurable artifacts onto the polymer thin-film surfaces.

3. RESULTS AND DISCUSSION

The specular reflectivity of the bare stainless steel surface is shown in Figure 2 together with a theoretical fit. In order to make a good fit, a 14.5 nm surface diffuseness was included and this value is rather consistent with the AFM result indicating a 14 .4 nm (RMS) roughness. For the PS/PVME coated samples the as-cast surface and the surface after three different annealing times, 7, 10 and 15 minutes were examined using a combination of XR, TRXF and AFM. The results indicated that the 7 and 10 minute annealing did not result in any significant surface roughness. Only the results from the as-cast and the 15 minute annealed samples will be included and discussed.

The AFM results of the as-cast and the annealed sample surfaces show a marked difference between these two surfaces (figure 3); the as-cast surface is almost featureless with a RMS roughness of 5.6 nm while the annealed one exhibit pointed peaks and bumps with a RMS roughness of 22.9 nm. These peaks are rather sparsely located across the whole sample with an average spacing of 30 μm. This annealing induced surface roughness manifests itself also in TRXF as shown in figure 4 where the TRXF results of these two surfaces and the bare one are given. The critical angle of the polymer blend used in this work is about 0.15° and is about 0.35° for the steel. For the bare surface a steep uprise of the fluorescence intensity once the incident angle went beyond 0.35° was not observed, this is due to the 14.4 nm RMS roughness of the bare stainless steel surface. Once coated with polymer film, the planarization of the polymer layer reduced the roughness to 5.8 nm. The fluorescent intensity is virtually zero at incident angle below 0.15° , the critical angle of the polymer. Above the critical angle the fluorescent intensity rose with incident angle and a periodic intensity modulation appeared. The origin of this modulation will be discussed later. As the polymer surface became rough by annealing, the fluorescent intensity below the critical angle became enhanced and the transition at the polymer critical angle became less well defined (Figure 4).

The XR results of the as-cast and the 15 minutes annealed surface are given in figure 5 together with their theoretical fits. The abscissa of this figure is Q_z, the magnitude of x-ray momentum transfer along the thickness direction and defined as $(4\pi/\lambda)\sin\theta$. λ is the x-ray wavelength of 0.15406 nm and θ is the incident angle. For both the as-cast and the annealed surface the XR results were almost identical. Some oscillations in the reflected intensity appeared at Q_z greater than 0.021 $Å^{-1}$ corresponding to the critical angle of the polymer layer. There is a sharp downturn in the reflected intensity after Q_z of 0.05 $Å^{-1}$, corresponding to the critical angle of the stainless steel. The oscillations appeared between these two critical angles are a manifestation of optical coupling, i.e. at certain incident angles the thin polymer film forms a x-ray waveguide and the incident beam travels along the films hence the reflected intensity shows a minimum. This type of waveguide mode can be accounted for readily using the existing reflectivity modeling algorithm. The fitted results are also included in the above figure. The film thickness was found to be 216.95 nm and the surface diffuseness was 11.0 nm and 12.0 nm for the as-cast and the annealed surface respectively. It is noteworthy that the diffuseness of 11.0 nm for the as-cast film is much greater than 5.58 nm as measured by AFM. On the other hand the diffuseness of the annealed surface was 12.0 nm which is lower than the AFM result of 22.9 nm. For the annealed surface the peaks or bumps are rather sparsely distributed with an average distance of 30 μm and XR might simply be dominated by the flat regions among these bumps. The reason for the observed discrepancy between the AFM and XR results on surface roughness for the as-cast surface is unclear.

For surface coated samples their TRXF intensity is expected to be linearly proportional to the x-ray intensity beneath the coating. The wavefunction, hence the intensity of the x-ray can be deduced from the XR data. Actually the wavefunction along the thickness direction is a byproduct of the current XR fitting process [6]. The excitation or the x-ray intensity within the first 20 nm of the stainless steel surface was compiled and plotted together with the measured TRXF (figure 6). For the as-cast surface the measured TRXF correlates well with the calculated excitation intensity; the measured value is greater than the calculated one only by a seemingly constant value, probably due to a constant background noise. The observed oscillations at incident angle greater than 0.15° are reproduced well by the calculation with the exception of the first three tightly spaced ones. All the TRXF data were collected with rather coarse spacing and fine spacing oscillations are not expected to be resolved. For the annealed surface the calculated x-ray intensity does not follow closely the measured TRXF. The calculation predicts a negligible fluorescent intensity below 0.15° and a sharp increase at 0.15°. The measurement indicates a noticeable fluorescence even below 0.15° and the transition at 0.15° is rather smooth. These features in the measured TRXF results can be rationalized qualitatively by considering the deviation of the incident angle at local scale as put forth in the introduction section of this work. However, this simple reasoning is incompatible to the current XR modeling algorithm where the reflectivity is treated as a one dimensional event and surface roughness is treated as diffuseness. The notion of local incident angle is just not included in current XR treatment.

4. CONCLUSIONS

Angle-dependent total-reflection x-ray fluorescence, in conjunction with atomic force microscopy, was used to study the surface roughness of polymer thin films deposited onto a stainless steel substrate. The surface roughness of the polymer coating was induced

by the phase-separation between polystyrene and poly (vinyl methyl ether) . The TRXF results provided discernible results between the smooth and the rough surface. For a surface with smooth coating, the TRXF result can be predicted reasonably well using data deduced from XR. For rough coating, TRXF provides additional information outside the scope of the current XR technique.

5. REFERENCES

1. R. Klockenkamper, Total-reflection X-ray Fluorescence Analysis, (John Wiley and Sons, New York, 1997).
2. K. Tsuji, T. Yamada, T. Utaka, and K. Hirokawa, J. Appl. Phys. **78** (2), 969 (1995).
3. D.K.G. de Boer, Phys. Rev. B **53** (10), 6048 (1996).
4. W. L. Wu and W. Wallace, to appear on *the Journal of Vacuum Science and Technology B.*
5. Q. Pan and R. J. Composto, Phase Separation Studies of Confined Thin Film Polymer Blends, edited by J. M. Drake, S.M. Troian, J. Klafter, R. Kopelman,(Materials Research Society, Pittsburgh, 1995). Vol. 366 p. 27.
6. J. F. Anker and C. F. Majkrzak, Neutron Optical Devices and Applications, SPIE, 1738, p260. (1992)

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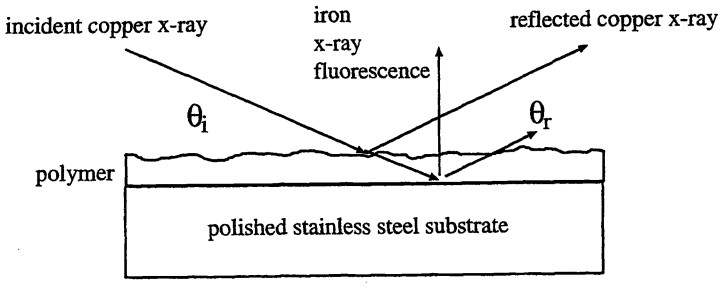

Figure 1. Schematic diagram of the smple configuration along with the beam paths for the specular reflection of the incident beam and the fluorescence of the iron inside the stainless steel substrate. The incident beam angle is given as θ_i while the specularly reflected beam angle is given as θ_r. The fluorescence is measured normal to the sample surface.

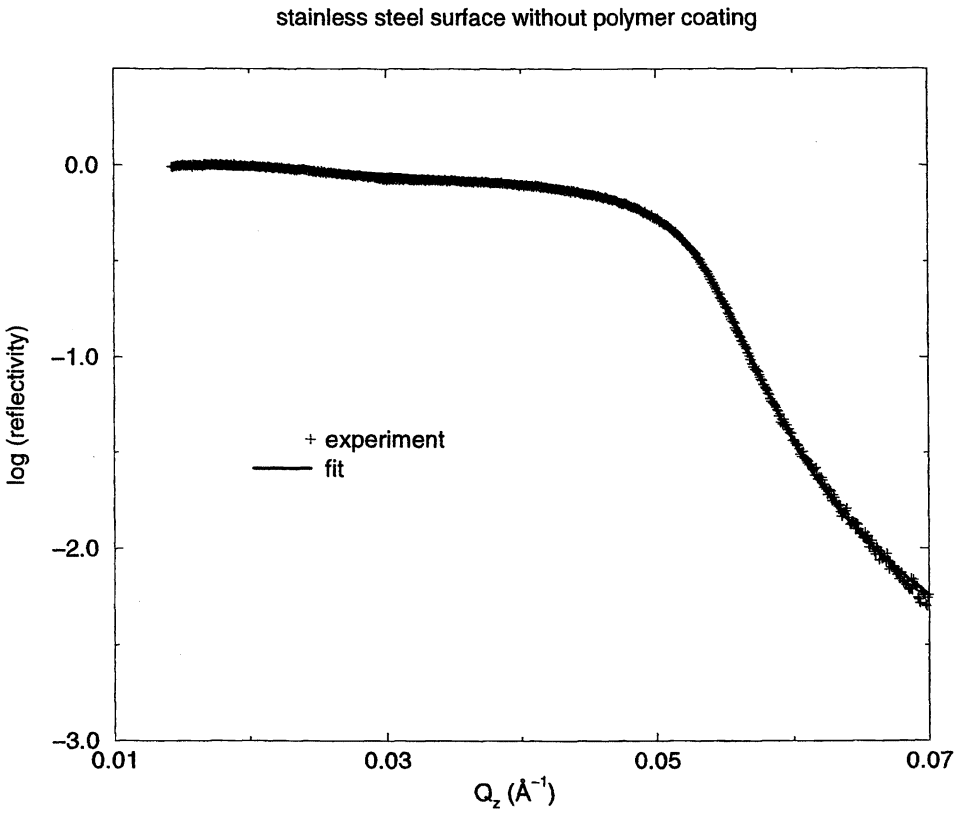

Figure 2. Specular x-ray reflectivity from the bare stainless steel surface and the theoretical fit.

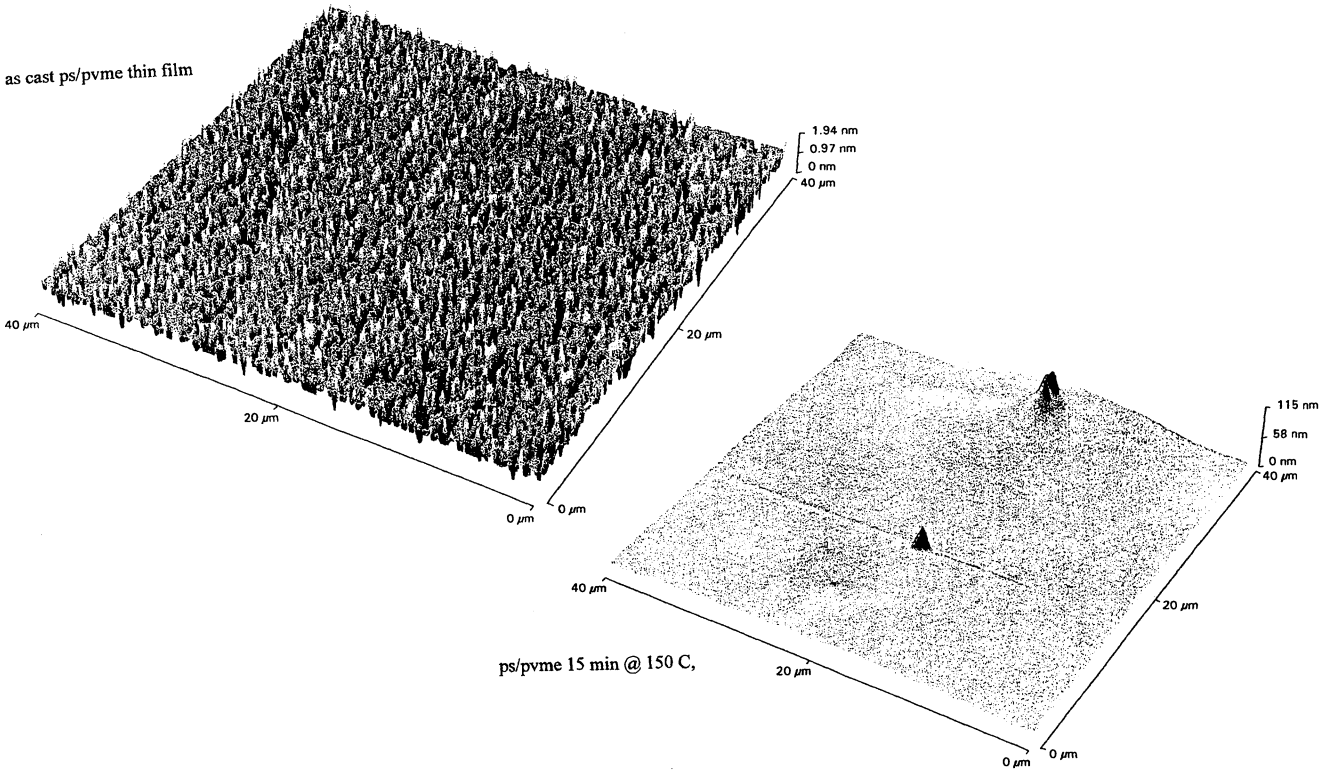

Figure 3. Non-contact-mode atomic force microscope image of the polystyrene / poly (vinyl methyl ether) film before and after annealing at 150 °C for 15 minute. Note the height scale of these two figures are grossly different; 1.94 nm and 115 nm for the unannealed and the annealed. The scanned region is 100 μm x 100 μm.

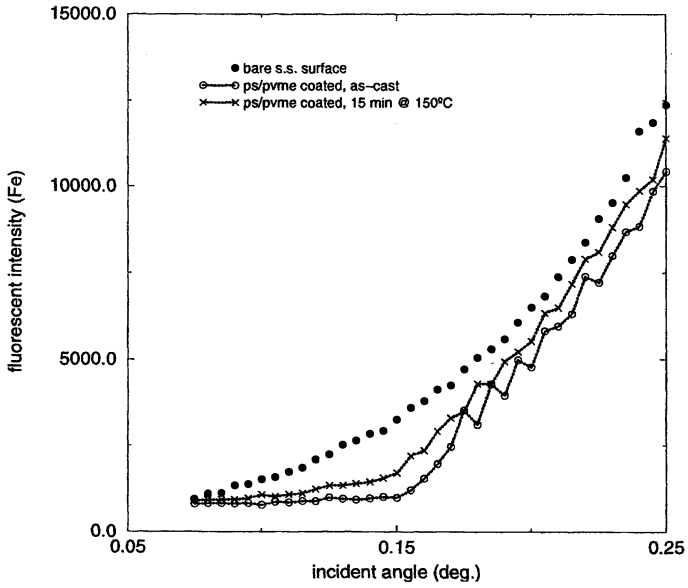

Figure 4. Angle-dependent total-reflection x-ray fluorescence from the stainless steel substrate for the phase-separated polystyrene / poly(vinyl methyl ether) blend films. For comparison, fluorescence from the bare substrate is also shown. Note the change in shape of the curves as a function of annealing time.

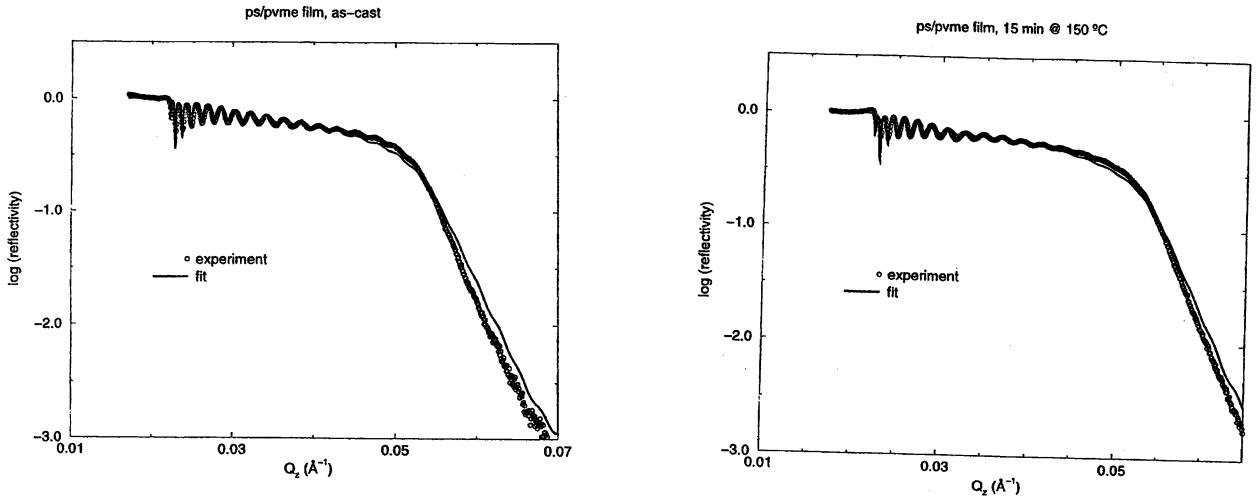

Figure 5. Specular x-ray reflectivities and their fits from the unannealed and the annealed polystyrene / poly (vinyl methyl ether) surfaces.

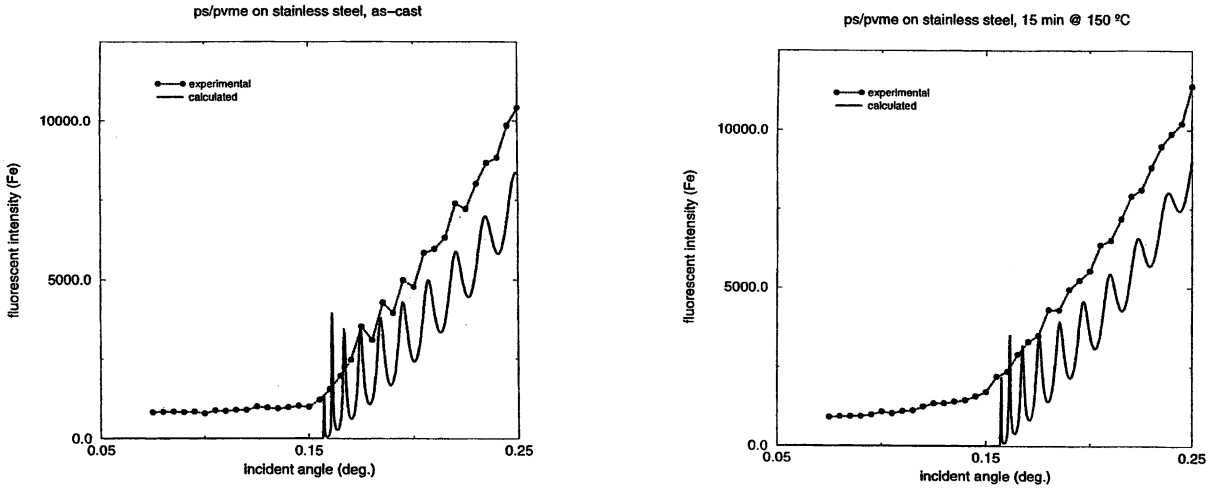

Figure 6. Angle-dependent total-reflection x-ray fluorescence and the calculated x-ray intensity within the top 20 nm layer of the stainless steel substrate from theunannealed and the annealed samples.