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Determination of modulation period of nano-multilayer coatings by low-angle X-ray methods

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Foreword

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This document was prepared by Technical Committee ISO/TC 107, *Metallic and other inorganic coatings*, Subcommittee SC 9, *Physical vapor deposition coatings*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Nano-multilayer coatings by physical vapor deposition (PVD), which possess high coating-substrate adhesion, high hardness and good wear resistance, corrosion resistance and conductive resistance, have been widely applied on tools, moulds, microelectronics and other important parts to improve their service life. Nano-multilayers formed by depositing two materials alternately at nanometer scale have attracted considerable interest due to their superior physical and chemical properties. The modulation period refers to the thickness of these two alternate layers.

Based on the chemical compositions, the main nano-multilayer coatings involve metal/metal, metal/ceramic and ceramic/ceramic systems such as Cu/Ni, Cu/W, Cu/Ag, Ti/TiN, Cr/CrN, Zr/ZrN, TiN/CrN, CrN/AlCrN, TiC/TiCN and CrAlN/AlCrTiSiN. The key factor influencing the properties of nano-multilayer coatings was previously the modulation period, which has an important effect on properties including hardness, toughness, electromagnetic and optical property. For example, as the modulation period decreases, the hardness of the nano-multilayer coatings increases. At present, the high-resolution projection electron microscope (HR-TEM) and the X-ray methods including the X-ray reflectivity (XRR) and glancing incident X-ray diffraction (GIXRD) are the two common methods for determining the modulation period of the nano-multilayer coatings. X-ray methods are more suitable for determination of the modulation period due to the advantages of being non-destructive, statistical, convenient and accurate compared with HR-TEM.

However, there is not yet any standard to qualify the modulation period of these nano-multilayer coatings, which limits their further development.

Thus, the motivation of this document is to prescribe the calculation of the modulation period of the nano-multilayer hard coatings and the measurement conditions of X-ray methods. The modulation period is an important technical indicator of the nano-multilayer coatings, which can also provide the communication bridge for customers who want to use the coatings, tool coater and analytic service provider. This document can be used for quality assurance of products with nano-multilayer coatings.

Determination of modulation period of nano-multilayer coatings by low-angle X-ray methods

1 Scope

This document specifies the substrate conditions and testing of the modulation period (including the principles for low-angle X-ray methods, the requirements of the coatings, the requirements for X-ray measuring apparatus, the calibration of apparatus and samples, and the testing conditions and calculation process) of nano-multilayer coatings by low-angle X-ray methods including X-ray reflectivity (XRR) and glancing incident X-ray diffraction (GIXRD).

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Substrate conditions

Considering that the roughness of industrial tools or moulds is normally not the roughness required, it is necessary to supply testing samples with the same substrate and surface condition. The roughness of the substrate of testing samples should be less than 50 nm of peak-to-valley or less than 5 nm RMS (route-mean-square) before the coating process. The substrate of testing samples should be cleaned by using the ultrasonic agitation procedure: immersion in a correct solution to remove hydrocarbons and others surface contaminants.

5 Testing of modulation period

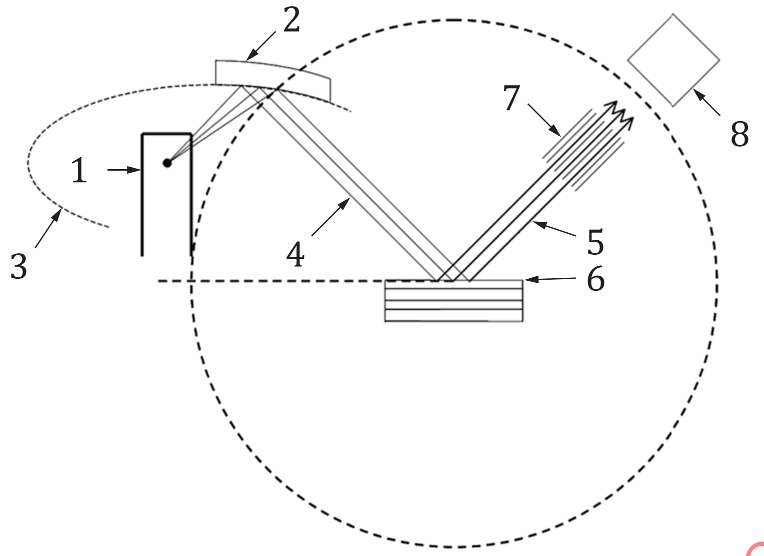
5.1 Principle for low-angle X-ray methods

5.1.1 General

The X-ray methods in this document consist of X-ray reflectivity (XRR) and glancing incident X-ray diffraction (GIXRD).

5.1.2 XRR method

When X-rays are irradiated on to the sample at very low angles, and the angle of irradiation is gradually increased beyond a certain angle called critical angle, X-rays are reflected from the interfaces of the sample and give rise to interference fringes. The periodicity of the fringes is proportional to the thickness of the modulation period. The modulation period can then be calculated by a specific calculation. Figure 1 shows the typical schematic diagram of the XRR method.



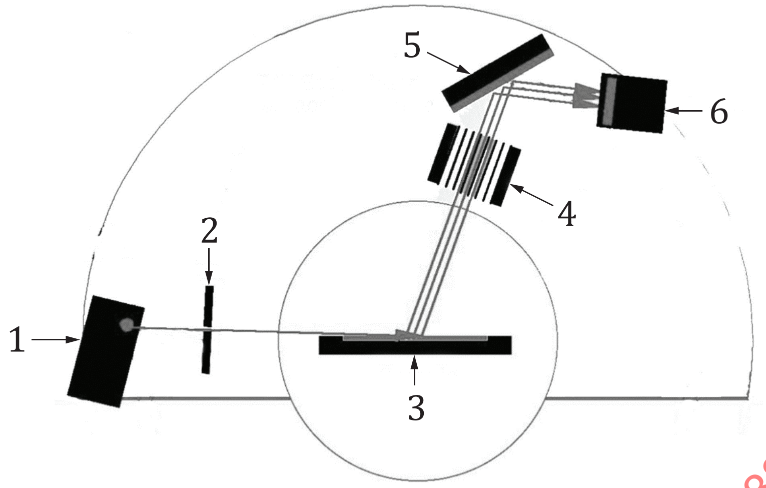
Key

1 X-ray tube
2 mirror
3 parabola
4 parallel X-ray beam
5 parallel X-ray beam
6 sample
7 soller slit
8 X-ray detector

Figure 1 — Schematic diagram of the XRR method

5.1.3 GIXRD method

GIXRD is a special XRD technology, for which the incident angle α is fixed. For nano-multilayer coating, the periodic modulation interfaces also cause the diffraction phenomenon in the low angle range (2θ= 0,3° to 10°, where θ is the peak position corresponding to the n^{th} order of the reflection). When X-rays are irradiated onto the sample at a low angle, diffraction fringes appear as the diffraction conditions are met. The modulation period can then be calculated by specific calculation. Figure 2 shows the schematic diagram of the GIXRD method. For the GIXRD method, the incident angle α is fixed.



Key

1 X-ray source
2 slit
3 sample
4 soller slit
5 LiF-secondary monochromator
6 detector

Figure 2 — Schematic diagram GIXRD method

5.1.4 Calculating formula

After obtaining the XRR or GIXRD pattern, the modulation period is calculated by the following modified Braggs-law, Formula (1):

$$\sin^2(\theta)=(\frac{n\lambda}{2\Lambda})^2+2\delta \quad (1)$$

where

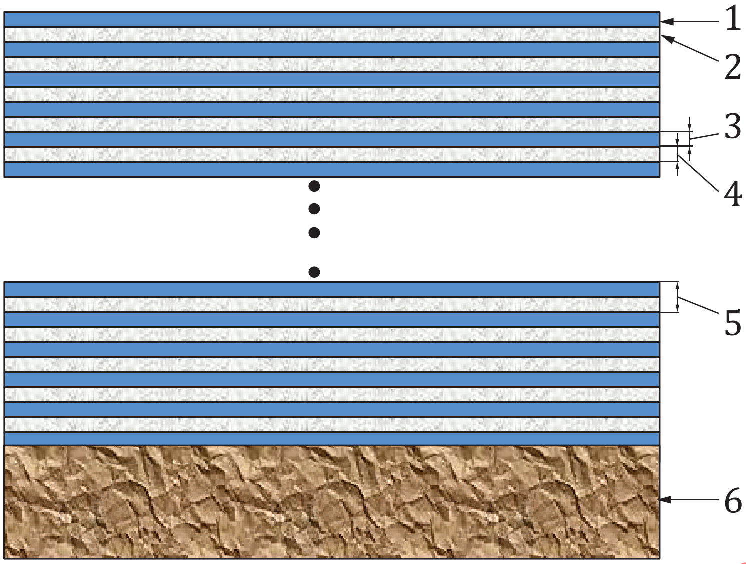
θ is the peak position corresponding to the n^{th} order of the reflection;

λ is the wavelength of X-ray;

δ is the deviation of the average refractive index of the film;

Λ is the modulation period.

The nano-multilayer coatings with modulation structure comprise two kinds of layers, in which every two adjacent layers constitute a unit and the thickness is called the "modulation period" ($\Lambda = \lambda_A + \lambda_B$, where λ_A and λ_B are the thickness of the A layer and B layer, respectively.) Λ is less than 200 nm or than a super-lattice coating, as shown in Figure 3.



Key

1 A layer
2 B layer
3 λ_A
4 λ_B
5 Λ
6 substrate

Figure 3 — Schematic diagram of the periodic structure of multi-layer coatings

5.2 Specifications concerning the coated sample

5.2.1 Size specifications for the coated sample

The coated sample should have a flat area of at least 10 mm in diameter for the measuring spot, in order to ensure a sufficient reflecting or diffraction area and volume. Considering that microelectronics generally do not have sufficiently large, flat and homogenous areas measuring 10 mm × 10 mm, an alternative choice of flat testing sample with the same substrate material and surface condition can be applied.

5.2.2 Periods specifications for the coated sample

The periods of the coated sample should be less than 200 nm because the period of 200 nm is beyond the resolution limit of the diffraction instrument.

5.2.3 Surface roughness requirements of the coated sample

Surface roughness, R_{pk}, of the nano-multilayer coating has an important effect on the determination of the modulation period.

a) When the surface roughness, R_{pk}, is more than 0,05 µm, the XRR method is unreasonable due to excessive scattering, and GIXRD technology can be used.

b) When the surface roughness, R_{pk}, is less than 0,05 µm, both XRR and GIXRD are used. In comparison to GIXRD, XRR is more accurate for measuring the modulation period of nano-multilayer.

5.3 Specifications for X-ray measuring apparatus

5.3.1 Apparatus configuration

5.3.1.1 Four-circular apparatus is necessary, which facilitates the rotation of the axes.

5.3.1.2 Sample holder, with adjustable height is also necessary.

5.3.2 Beam conversion device

5.3.2.1 A beam conversion device such as a Goebel mirror (GM) is used to convert the diverging beam from the X-ray generator to the parallel light beam with a fixed breadth. In addition, the intensity of obtained pattern is more than 1 000 000 000 counts per second (cps) with low background by using the GM device.

5.3.2.2 Incident slits with 0,1 mm, are inserted between the sample holder and the GM to tune the resolution of the apparatus. However, the inserting of these slits decreases the intensity of the obtained pattern.

5.3.2.3 For the reflection or diffraction information receiving section, receiving slits between the sample holder and detector are also used to control the intensity and resolution of the pattern.

5.3.3 Radiation sources and filters

For testing of the coated samples, Mo, Cu and Co targets are used. The filters are used to get a monochromatic Kα light, and the common X-ray targets for testing. The corresponding filters are listed in Table 1.

Table 1 — Common X-ray targets for testing and the corresponding filters

Target	Kα nm	Filter
Mo	0,071 07	Zr
Cu	0,154 18	Ni
Co	0,154 18	Fe

NOTE Kα is the ray produced by the transition of an electron from the L to the K shell for the K radiation.

5.4 Calibrating of apparatus

X-ray measuring apparatus shall be carefully calibrated before testing to eliminate or reduce the equipment error.

Si plate with a size of 10 mm × 10 mm were used to calibrate the apparatus.

The requirements of the Si standard sample are the following.

a) The Si powder is selected as the calibration sample.

b) The Si powder shall be annealed without micro-strain.

c) The mean size of the annealed Si powder shall be more than 100 µm.

The testing conditions and operation procedures are given in 5.5.

When the θ ($\theta = |\theta_{Si\ power} - \theta_{Si}|$, where $\theta_{Si\ power}$ and the θ_{Si} represent the degree (at a low degree) of the Si standard sample and the International Centre for Diffraction Data of Si, respectively) < 0,001°, the apparatus calibration is complete.

Before the XRR and GIXRD examination, the X-ray light path and samples should be calibrated, which can provide high accuracy.

5.5 Testing conditions

5.5.1 Operating voltage: 20 kV to 50 kV. 40 kV is recommended.

5.5.2 Operating current: 20 mA to 40 mA. 30 mA is recommended.

5.5.3 Scanning range (2θ): 0,3° to 10°.

5.5.4 Scanning step: ≤ 0,001°.

5.5.5 Scanning speed: ≤ 0,1°/ min

5.5.6 Incident angle (α): 0,2° to 5°. 0,5° is recommended.

5.5.7 The pattern intensity is dependent on many factors, such as scanning speed, scanning time, operating voltage and current, types of receiver, slits and detector. The intensity of the obtained pattern should be sufficient to fit and obtain the accurate degree of 2θ.

5.6 Test and calculation procedure

The steps to calculate the modulation period of nano-multilayer coating by XRR or GIXRD are as follows.

1) Calibration of the X-ray light path and samples.

2) Selection of incident and receiving slits with 0,1 mm.

3) Selection of Cu as the radiation source and Ni filter.

4) Operating voltage: 40 kV; operating current: 30 mA.

5) Scanning range (2θ): 1,5° to 10°; scanning step: 0,001°; scanning speed: 0,05°/min; incident angle (α): 0,5°. Then, running of the test program.

6) Obtention of the XRR or GIXRD pattern of the nano-multilayer coatings.

7) Fitting of the obtained XRR pattern by using Formula (1), regressing the $\sin^2(\theta)$ and n^2(n = 1, 2, 3, 4……).

The examples of the determination process of modulation period by XRR are listed in Annex A.

