National Institute of Standards and Technology

Certificate

Standard Reference Material® 2135c

Ni/Cr Thin Film Depth Profile Standard

This Standard Reference Material (SRM) is intended primarily for calibrating sputtered depth scales and erosion rates in surface analysis. Its periodic structure, consisting of eight well-defined metal/metal interfaces, can be used to obtain accurate calibration at a number of depths. SRM 2135c is certified for total Chromium (Cr) and Nickel (Ni) thickness, single element layer-to-layer uniformity, Ni and Cr bilayer uniformity (periodicity) and single layer thickness [1-3]. Certified thickness values, expressed in units of mass/area, are given in the section entitled Certified Values and Uncertainties.

A unit of SRM 2135c consists of nine alternating metal thin-film layers, five layers of pure chromium and four of pure nickel, on a polished silicon (100) substrate. The individual layers have thicknesses that are nominally 57 nm for Cr and 56 nm for Ni. The area of the specimen that is certified is determined by the full width of the substrate (1.0 cm) and a length of 2.0 cm centered on the 2.54 cm length of the substrate (see Figure l).

Expiration of Certification: The certification of this SRM is deemed to be indefinite within the measurement uncertainties specified provided the SRM is handled, stored, and used in accordance with the instructions provided in this certificate. However, the certification will be nullified if the SRM is altered, contaminated or damaged.

This SRM was fabricated by RF magnetron sputtering at COMSAT Laboratories, Clarksburg, MD, under the direction of L.B. Holdeman and E.R. Sparks.

Auger Sputter Depth Profile analyses were performed by L. Tanovic, N. Tanovic, and J. Fine of the NIST Surface and Microanalysis Science Division. X-ray Fluorescence (XRF) Spectrometry measurements were performed by P.A. Pella and A.F. Marlow of the NIST Analytical Chemistry Division. Inductively Coupled Plasma (ICP) Spectrometry measurements were performed by R. Saraswati, L.J. Wood, and M.S. Epstein of the NIST Analytical Chemistry Division. Secondary Ion Mass Spectrometry (SIMS) Sputter Depth Profile analyses were performed by D.S. Simons and P.H. Chi of the NIST Surface and Microanalysis Science Division.

Statistical consultation was provided by K.R. Eberhardt and J.H. Yen of the NIST Statistical Engineering Division.

The overall direction and coordination of the technical measurements leading to certification were performed by J. Fine of the NIST Surface and Microanalysis Science Division.

The technical and support aspects concerning the preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by R.J. Gettings.

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CERTIFIED VALUES AND UNCERTAINTIES

A. Total Cr and Total Ni Thicknesses: The total certified thickness and expanded uncertainties of the five Cr layers and the total thickness of the four Ni layers were determined by XRF and ICP using a gravimetrically calibrated reference.

Element	Certified Total Thickness
Cr	206.3 μg/cm^2 ± 13.8 μg/cm^2
Ni	197.4 μg/cm^2 ± 9.6 μg/cm^2

The uncertainties of the certified total thicknesses are expressed as expanded uncertainties at the 95 % level of confidence, and are calculated according to the guidelines described in Reference [4]. An expanded uncertainty is calculated as $U = ku_c$, where the coverage factor, $k = 2$, corresponds to 95 % confidence, and where u_c is intended to represent, at the level of one standard deviation, the measurement uncertainty. The stated uncertainties are due to three components: uncertainty due to ICP calibration, between-specimen differences (obtained by wide field XRF), and within-specimen differences (obtained by small field XRF), see Tables l and 2. Additional information regarding within-specimen uniformity was provided by SIMS analysis. The within-specimen differences indicate that variations exist in the total Cr and Ni thicknesses over the central 1.0 cm x 2.0 cm certified area.

B. Single Element Layer-to-Layer Uniformity and Ni + Cr Bilayer Uniformity (periodicity): Layer-to-layer thickness uniformity of the Cr and Ni layers was determined by measuring the ion bombardment time required to remove individual layers of the same element by sputter erosion. This time was obtained by monitoring the surface composition by Auger spectroscopy using 50 % intensity criteria (see Figure 2) during sputter profiling. Analysis was obtained over a region of the surface about 10 μm in diameter. The uniformity of the Ni + Cr bilayer removed, was determined in a similar manner.

Type of Layer	Certified Layer-to-Layer Uniformity (relative standard deviation in %)
Single Cr Layer	$0.8\ ^{+2.1}_{-0.6}$
Single Ni Layer	$0.9\ ^{+1.5}_{-0.6}$
Bilayer	$0.6\ ^{+2.2}_{-0.5}$

The uncertainties in the certified values are expressed as 95 % confidence intervals. These calculations involved several steps. First, for a particular element or bilayer, the layer-to-layer relative standard deviations obtained from the different batches using Auger spectroscopy were pooled into a sample and re-expressed using a logarithmic transformation. If □ and u_y are the sample mean and standard deviation of the transformed values, then the certified relative uniformity is calculated as exp (□) and the confidence interval has the form exp (□ ± k u_y), where the coverage factor, $k = 2.365$, is determined from the Student's t-distribution with 7 degrees of freedom and 95 % confidence. As shown in the uncertainty statements, such confidence intervals are not symmetric about the certified values.

C. Single Layer Thickness: The certified thickness for single layers of a given element was obtained from the total layer thickness for that element and the number of layers present.

Element	Certified Single Layer Thickness
Cr	41.3 μg/cm^2 ± 2.8 μg/cm^2
Ni	49.4 μg/cm^2 ± 2.6 μg/cm^2

The uncertainty of a certified single layer thickness is expressed as an expanded uncertainty at the 95 % level of confidence, and is calculated according to the guideline described in Reference [4]. An expanded uncertainty is

calculated as $U = ku_c$, where the coverage factor, $k = 2$, corresponds to 95 % confidence, and where u_c is intended to represent, at the level of one standard deviation, the measurement uncertainty. The uncertainty of the single layer thickness of an element is determined by combining the uncertainty of the average total thickness of that element, which is described in section A of this certificate, and the uncertainty of the layer-to-layer uniformity of that element, which is described in section B.

Structure Description: The silicon substrate was lightly sputter etched *in situ* to obtain a clean, amorphous surface for layer deposition. Metal thin-film structures were produced by RF magnetron sputter deposition beginning with a layer of Cr. This was followed by alternate layers of Ni and Cr with Cr forming the outermost layer, (see Figure 1). Dimensions of the substrate are 1.0 cm x 2.54 cm x 0.04 cm, with the films deposited on the largest surface. The layered face is the more reflective surface.

Instructions for Use: Information on material composition as a function of depth at surfaces and interfaces can be obtained by monitoring the elemental surface concentration as successive surface layers are sputter-removed at known rates by ion bombardment. SRM 2135c is intended primarily to provide a means for determining sputtered depths as well as sputter erosion rates in surface analysis. Determination of sputtered depth can be made at seven depths with this one SRM using metal/metal interfaces of known spacings. The well-ordered structure of this SRM makes it useful for verifying correct instrument operation, monitoring ion beam current-density stability, and producing sputtering conditions that achieve maximum interface resolution.

The thin-film metal layers can be distinguished as the more reflective surface of this SRM. The outer Cr layer is not intended for depth calibration purposes but can be useful for ion beam current measurement and specimen alignment. Sputtered depth and rate measurement can begin at the outermost Cr/Ni interface using, for example, 50 % of maximum elemental signal intensity as a reference point for layer removal measurement. Greater accuracy of sputter removal times and depths can be obtained from a periodicity measurement for the removal of a Ni + Cr bilayer pair.

An example of an Auger sputter depth profile obtained with this SRM is shown in Figure 2.

Relative Sputtering Rates and Yields of Ni and Cr Using Argon Ion Bombardment (not certified):

Ion Energy (keV)	Ni Rate*/Cr Rate	Ni Yield**/Cr Yield
1.0	1.03	1.12
2.0	1.07	1.17
3.0	1.09	1.20
4.5	1.09	1.20

*Rate is expressed in units of length/time
**Yield is expressed as number of atoms sputtered per incident ion

Expressing Layer Thicknesses in Units of Length: The certified layer thicknesses could be converted into units of length (nm) if the densities of the layers were known. As these densities are not known, an approximate thickness can be derived by using the known bulk densities for Cr (7.19 g cm^{-3}) and Ni (8.9 g cm^{-3}); the values so obtained are 57 nm for Cr and 56 nm for Ni.

Cautions to User: The usefulness of SRM 2135c for sputter rate calibration depends on maintaining a constant ion current density at the point of analysis. Care must be taken to ensure that the ion beam current remains constant and that the beam position on the specimen remains fixed.

Precise determination of a reference point for layer removal measurement requires that the single layer profiles be clearly resolved (i.e., flat topped profiles) so that the sputtered interface regions are well defined.

Foreign surface particulates should be removed before profiling by use of clean, pressurized gas; it is not advisable to use solvents for cleaning as they can leave some residue.

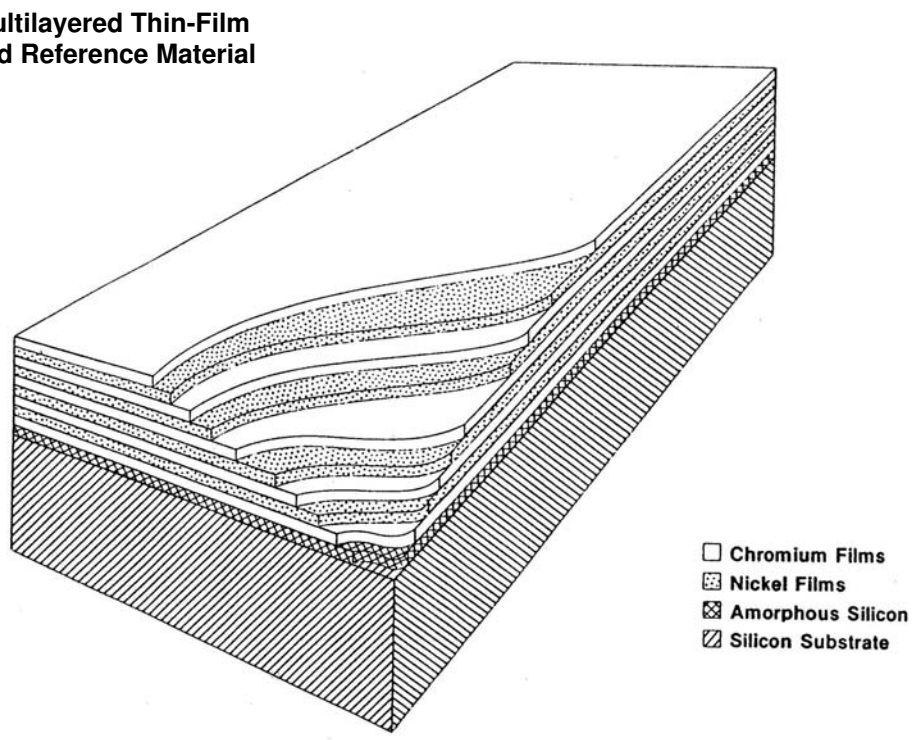

Figure 1. Sectional view of the thin-film multilayered SRM structure. The nominal thickness of each Cr layer is 57 nm and each Ni layer is 56 nm.

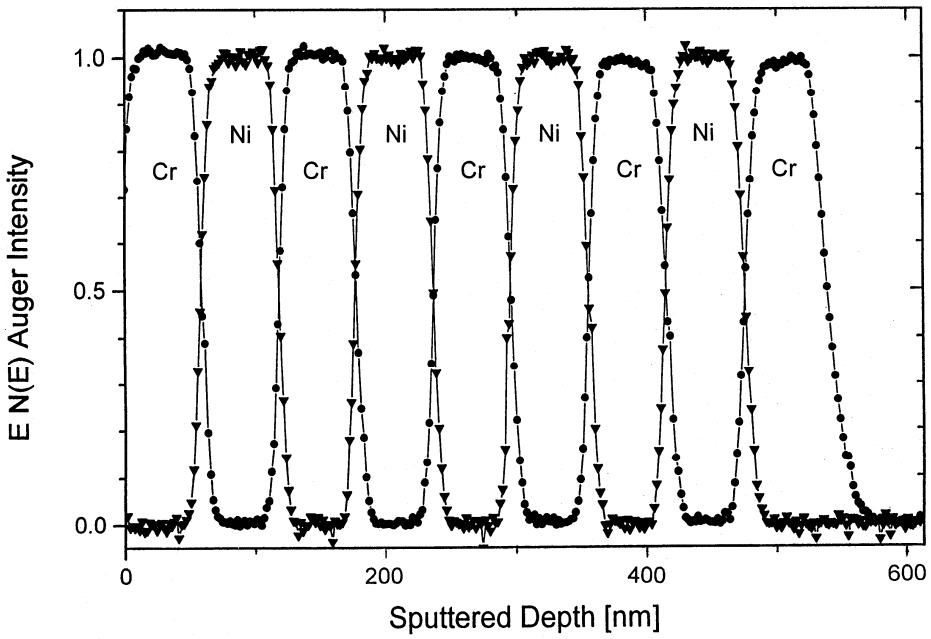

Figure 2. Auger sputter depth profile representative of SRM 2135c obtained using 1 keV argon ion bombardment. The pure Ni and Cr Auger intensities shown have been normalized.

Table l. Identification of Uncertainties: Total Thickness of Cr

Source	Relative Standard Uncertainty
ICP Measurement	1.33 %
Between Specimen Differences (Wide Field-XRF)	1.12 %
Within-Specimen Differences (Small Field-XRF)	2.85 %
Combined Standard Uncertainty, u_c	3.34 %
Coverage Factor, k	2
Expanded Uncertainty, $U = ku_c$	6.68 %

Table 2. Identification of Uncertainties: Total Thickness of Ni

Source	Relative Standard Uncertainty
ICP Measurement	1.52 %
Between-Specimen Differences (Wide Field-XRF)	1.46 %
Within-Specimen Differences (Small Field-XRF)	1.22 %
Combined Standard Uncertainty, u_c	2.44 %
Coverage Factor, k	2
Expanded Uncertainty, $U = ku_c$	4.88 %

REFERENCES

[1] Fine, J. and Navinsek, B., "Characterization of NBS Standard Reference Material 2135 for Sputter Depth Profile Analysis," J. Vac. Sci. Technol. **A3**, p. 1408, (1985).

[2] Fine, J., Lindfors, P.A., Gorman, M.E., Gerlach, R.L., Navinsek, B., Mitchell, D.F., and Chambers, G.P., "Interface Depth Resolution of Auger Sputter Profiled Ni/Cr Interfaces: Dependence on Ion Bombardment Parameters," J. Vac. Sci. Technol. **A3**, p. 1413, (1985).

[3] Fine, J. and Navinsek, B., "An NBS Standard Reference Material for Depth Profile Analysis," Surf. Interface Anal. **11**, p. 542, (1988).

[4] *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, lst Ed. ISO, Geneva, Switzerland, (1993): see also Taylor, B.N., and Kuyatt, C.E., "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results," NIST Technical Note 1297, U.S. Government Printing Office, Washington DC, (1994).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: Telephone (301) 975-6776 (select "Certificates"), Fax (301) 926-4751, e-mail srminfo@nist.gov, or via the Internet http://ts.nist.gov/srm.