Auger Electron Spectroscopy of Oxidized Titanium Overlayers: Speciation of Homogeneous and Heterogeneous Samples

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Contents

Abstract

Auger electron spectroscopy (AES) is often used for the determination of the quantitative composition and the speciation of the materials under investigation. The present work illustrates the quantitative analysis of titanium oxides and its application to the characterization of a partially oxidized titanium overlayer on top of a copper substrate. The quantitification procedure described provides an average composition of the surface area investigated. Care has to be taken to convert this composition into an information about the chemical species present at the sample surface because the observed fine structures of the AES spectra cannot be correlated unambiguously with the chemical species present. The AES spectra are not suited to distinguish conclusively between a homogeneous composition of the analyzed volume and the presence of a mixture of several titanium species. Additional information is required for a final distinction between the two possibilities, which can be achieved, for example, by X-ray photoelectron spectroscopy (XPS).

Augerelektronen-Spektroskopie an oxidierten Titan-Deckschichten:
Speziation homogener und heterogener Proben

Zusammenfassung

Die Augerelektronen-Spektroskopie wird oft zur Bestimmung der quantitativen Zusammensetzung und zur Ermittlung der in der Probe vorhandenen chemischen Spezies eingesetzt. Die vorliegende Arbeit beschreibt die quantitative Analyse von Titanoxiden und deren Anwendung zur Charakterisierung einer partiell oxidierten Titan-Deckschicht auf einem Kupfersubstrat. Das beschriebene Verfahren erlaubt es, eine mittlere Zusammensetzung der erfaßten Oberfläche zu ermitteln. Bei der Interpretation dieser Zusammensetzung in Hinblick auf die Art der chemischen Spezies, die sich an der Probenoberfläche befinden, ist eine vorsichtige Vorgehensweise angebracht, weil die Feinstruktur der Augerspektren nicht zweifelsfrei mit den vorhandenen chemischen Spezies korreliert werden kann. Die Augerspektren sind nicht geeignet, eindeutig zwischen einer homogenen Zusammensetzung des analysierten Volumens und dem Vorhandensein einer Mischung mehrerer Titanspezies zu unterscheiden. Um diese Unterscheidung abschließend durchführen zu können, werden zusätzliche Informationen benötigt, die zum Beispiel mittels röntgenstrahlinduzierter Photoelektronen-Spektroskopie (XPS) erhalten werden können.

I.   Introduction

Electron induced Auger electron spectroscopy (AES) is commonly used as a surface sensitive technique that allows the quantitative analysis and, in addition, the speciation of the uppermost atomic layers of solid materials. The possibility of combining AES with ion beam induced erosion of the materials' surfaces allows, as an important additional feature, the determination of in-depth distributions of the materials' components. Therefore, the combination of AES and ion bombardment gives access to the sample surface as well as to a surface-near region of up to a few micrometers thickness.

The standard approach to quantification and to speciation is the determination of (relative) elemental sensitivity factors and/or the comparative analysis of standard materials of known composition. The application of elemental sensitivity factors permits the analysis of all kinds of samples but suffers from the influences of matrix effects. The second approach requires the availability of sufficiently characterized standards and is, therefore, better suited for the analysis of less complex systems. However, the access to chemical information (speciation) is better in the latter case.

One of the important examples for the application of AES in materials science is the investigation of titanium metal, of its alloys, and of its reaction products with various reactants. These investigations are of interest in context with bonding and adhesion properties of titanium containing materials (1), with the corrosion resistance of titanium alloys (2), and with the reaction (e.g. gettering) behavior of titanium in general (3) and for the production of wear resistive compounds (1 a,4). More basic investigations using AES dealt with problems of the speciation (3 b,5) and quantification (3 c,6) of titanium metal and its oxides and with the explanation of specific spectral features (7). Additional work was performed for understanding the influences on the AES spectra of electron beams used for the excitation of AES spectra and of ion beams used for the removal of surface near material by sputtering (6 c,8).

The intention of the present work is to describe the results of an attempt to speciate and to quantify partially oxidized titanium layers, which originate from the treatment of titanium coated copper substrates with alkaline hydrogen peroxide solutions. Speciation and quantification were based on an approach already described in literature (3 c,6 c), which makes use of a correlation of Auger peak intensity ratios with the known stoichiometry of reference materials. The

major aim of this publication is to show that this approach is not straight-forward as soon as the lateral sample composition is heterogeneous. In this case the interpretation may be erroneous unless independent methods e.g. X-ray photoelectron spectroscopy (XPS) permit additional characterization.

II. Experimental

Titanium coated copper plates with a thickness of the titanium overlayer of about one micrometer are used as support for the X-ray sensitive polymer (polymethyl-methacrylate) in deep-etch synchrotron radiation lithography (11). To get a sufficient adhesion of the polymeric microstructures, which are produced by synchrotron irradiation and subsequent development, it is necessary to pretreat the support by chemical etching with alkaline hydrogen peroxide solution. It has been observed that the adhesion properties of these microstructures depend strongly on etch time.

The sample to be characterized consisted of a copper substrate, which was coated on one side with 1 μm of titanium metal by sputter deposition. Afterwards the sample was treated in an alkaline hydrogen peroxide solution (composition: 0.5 m NaOH, 0.2 m H_2O_2) for about 5 minutes at 65 °C.

To investigate the reason for the etch time dependent adhesion properties the etch time has been varied systematically and the effects of etching on structure and chemistry of the titanium overlayer have been followed by AES depth profiles (12). The observed variations of the depth profiles made it worthwhile to examine whether or not the AES spectra were suited for a quantification and speciation of the overlayer after etching.

Titanium dioxide, titanium sesquioxide, titanium monoxide, and titanium metal were choosen as reference materials. The titanium dioxide reference sample consisted of a thin layer (about 40 nm thick) of the oxide on an aluminum substrate. The oxidic overlayer was produced by reactive sputtering of titanium metal in an oxygen atmosphere (9). The use of titanium dioxide powder was not suitable because of charging of the sample under electron bombardment in AES analysis, which causes a line shift and eventually line broadening. Especially the latter effect is unwanted, if line shapes are to be investigated. We have observed that charging can be reduced by extended sputtering of the dioxide, supposedly due to the formation of a sufficiently conducting surface layer. However, the authors are

in doubt whether this treatment can eliminate line shape broadening effects with certainty. In contrast to the powder sample, the titanium dioxide overlayer formed by reactive sputtering showed no charging even without any pretreatment. In addition, an XPS analysis as well as X-ray diffraction indicated that substantial differences in composition between the powder and the thin layer sample were absent (9).

The suboxides of titanium consisted of powders (purchased from Ventron GmbH, Karlsruhe; stated purity 99 % metals basis) and were pressed to thin circular pellets of 8 mm diameter and about 0.5 mm thickness at a pressure of 10^3 N $\cdot$ mm^{-2}. Both compounds showed no evidence of charging due to their higher conductivities and could, therefore, be used as reference materials.

Titanium metal samples were made from 0.5 mm thin sheets. Any surface contaminations (adsorbed hydrocarbons, oxidic overlayer) were removed by ion bombardment.

The AES and XPS measurements were performed in a Vacuum Generators (VG) ESCALAB 5 electron spectrometer described in detail elsewhere (10). Samples of appropriate size were sticked to metal probes by adhesive and conducting silver paint, and were measured after introduction into the ultra-high vacuum system as soon as a base pressure of 10^{-9} mbar was achieved.

Auger spectra were recorded in the derivative mode at a constant retard ratio of ten, a modulation voltage of 2.0 eV and a time constant of the lock-in amplifier of 300 ms. Spectra acquisition and storage was controlled by a PDP 11/03 computer. The measured spectra resulted from the summation of several repetitive scans with a step width of 0.2 eV per channel and a scan speed of 17 channels per second.

Auger electrons were excited by electrons with a primary energy of 5 keV, a total current of 2.0 µA and a current density of 33 µA $\cdot$ mm^{-2}. The electron gun used was a VG LEG 100.

Ion bombardment for cleaning purposes was performed using a Leybold-Heraeus IQP 10/63 ion gun at a primary energy of about 5 keV and a current density of approximately 150 nA $\cdot$ mm^{-2}. Ion bombardment for depth profiling was achieved by a focussed ion beam (VG AG 61 ion gun, ion beam diameter approximately 100 µm) of 5 keV primary energy, a total beam current of 200 nA and a current density of approximately 250 nA $\cdot$ mm^{-2}.

XPS spectra were recorded by excitation with Al K α radiation (100 W X-ray power) in the constant analyzer pass energy mode. The pass energy was choosen to be 20 eV for the acquisition of the spectra of the major photoelectron lines. The spectra were digitized with a step width of 0.1 eV and a scan speed of about 25 channels per second. Normally, the spectra represent the sum of several repetitive scans.

III.   Results and Discussion

1.   Chemical oxidation of the titanium/copper sample

This chapter gives an example of a depth profile acquired after etching a titanium coated copper plate for about five minutes. After a short description of the in-depth distributions as compared to those of an unetched sample, the following two chapters illustrate the approach choosen for quantification and speciation and its short-comings with regard to the sample described in this chapter.

Fig. 1 a shows the depth profile of a Ti/Cu sample before etching. The in-depth distributions of the main constituents of the sample are represented by the peak-to-peak intensities of the corresponding differentiated Auger lines. The profile directly reflects the layered structure of titanium on top of copper. Both elements exhibit nearly constant signal intensities over the depth ranges of the overlayer and the substrate, respectively. Very close to the surface one observes an increase of the titanium signal intensities accompanied by a steep decrease of the O(KLL) intensity. This results from the fact that each titanium metal surface after contact with air is covered by a thin titanium dioxide layer. This layer is quickly removed by sputtering which leads to the observed variations of the signal intensities of titanium and oxygen.

It is remarkable that the oxygen signal intensity and thus the oxygen concentration does not vanish in the bulk of the titanium metal overlayer, but remains at an easily detectable level. This could, in principle, mean that during the formation of the overlayer by sputter deposition oxygen has been incorporated.

However, the sputter conditions used for the overlayer formation are believed to lead to a crystalline product which exhibits open grain boundaries (11 a,13). Therefore, not only the visible surface of the overlayer is oxidized during contact with air but also those grain boundaries within the overlayer, which are accessible

to the oxidizing agent. This will lead to the detection of certain amounts of oxygen also within the layer. In this latter case, however, oxygen is not distributed homogeneously, but concentrated at the oxidized open grain boundaries.
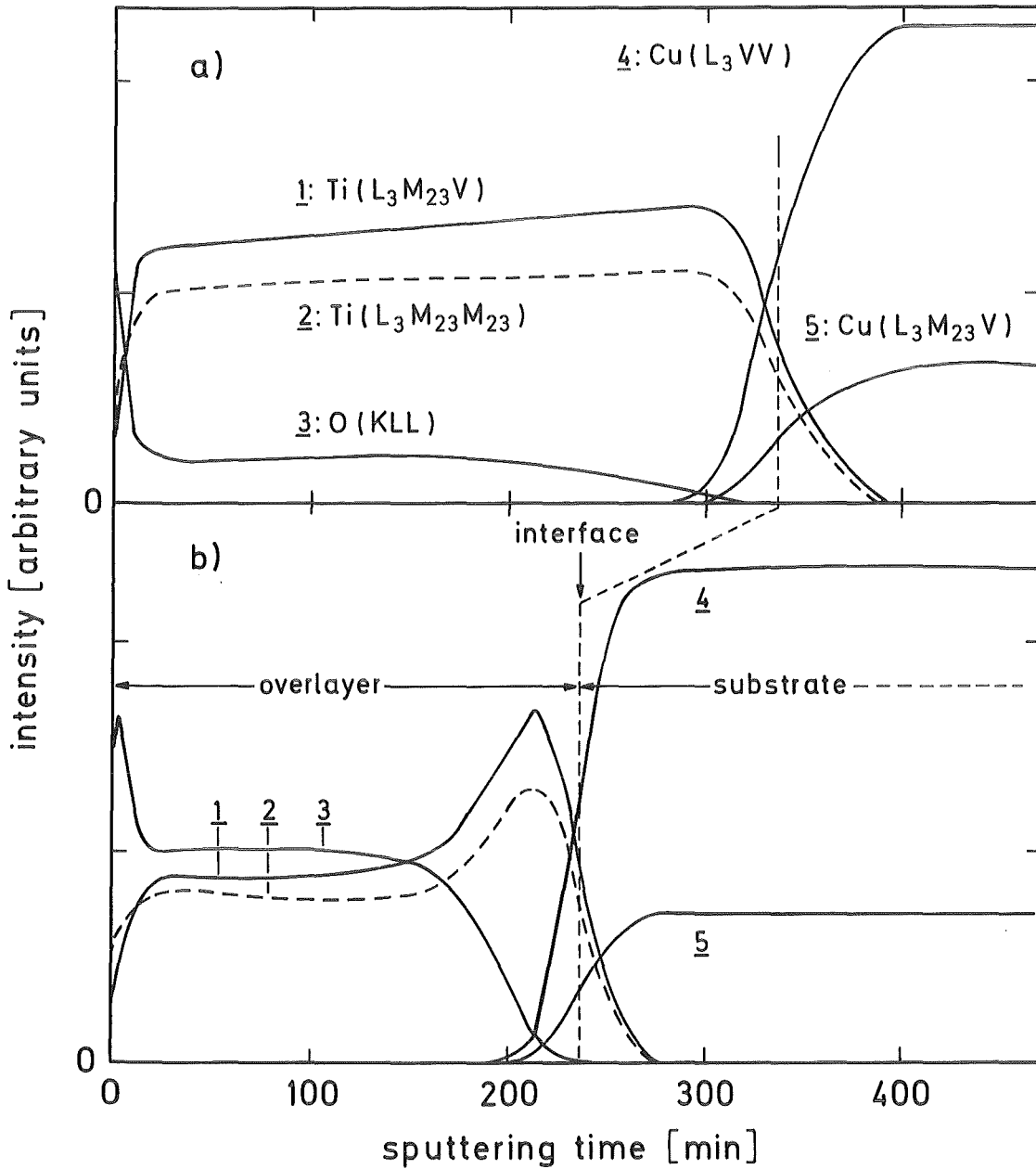

Fig. 1 Depth profile of Ti/Cu samples (a) before and (b) after oxidation with peroxide solution. One minute of sputtering time corresponds to the removal of about 2.8 nm of surface material.

For comparison, Fig. 1 b shows the depth profile of another Ti/Cu sample after treatment with peroxide solution for several minutes. Two major effects of the treatment can be evaluated directly from a comparison of the two profiles. The primary effect is that the overlayer has been reduced in thickness as indicated by the shorter sputtering time needed to reach the interface. In addition, comparison of the signal intensities of the O(KLL) transitions in both figures shows a significant increase of the oxygen content by the etching process, i.e., the oxidative attack leads to a partial dissolution of the overlayer and to a residue of undissolved titanium oxide.

The oxygen signal intensity passes a maximum close to the sample surface. It then drops to a value comparable to that of the titanium Auger lines remaining constant in the major part of the overlayer. The occurrance of a maximum indicates that the visible surface of the overlayer after peroxide treatment is covered with an oxidic layer thicker than the natural dioxide formed during air contact.

The existence of a plateau could be explained by a homogeneous partial oxidation of the titanium overlayer. However, the observed depth profile can also be explained by the presence of open grain boundaries, which may allow an attack of the peroxide solution at deeper parts of the overlayer. The increase of the titanium peak intensities and a corresponding decrease of the O(KLL) intensity shortly before the actual interface is reached, favour the second mechanism. In this case, the maxima of the titanium signal intensities would correspond to a region of the overlayer where the crystals have grown together so closely that the grain boundaries are not accessible any more to the peroxide solution (and to any other oxidizing agent, e.g. air; compare oxygen profile in Fig. 1 a).

2.   Characterization of reference materials

XPS spectra taken directly after introduction of the samples into the spectrometer showed that the surfaces of the metal and of the suboxides had been oxidized to titanium dioxide. Only in the case of the metal sheet a small additional signal was observed, which could be attributed to titanium metal originating from metal atoms underneath the dioxide overlayer. Therefore, three of the four samples could not be used "as received" for referencing purposes. It was necessary to lay bare the underlying materials, which is favourably done by ion induced sputtering in the ultra-high vacuum system of the electron spectrometer. However, titanium oxides are known to undergo preferential sputtering effects, which lead to the formation

of lower oxides in the surface near region. Titanium dioxide is partly reduced to the threevalent and the divalent oxidic state but not to the metal (8). Consequently, titanium sesquioxide should, in part, be converted to titanium monoxide, while the oxidation state of the latter is not affected by sputtering.

According to the observed reduction effects, homogeneously composed samples of the three titanium oxides, which are ion bombarded until sputter equilibrium is reached, exhibit surfaces, which are composed of the original oxide and the lower oxides (except, of course, in case of TiO). When using powder samples of the suboxides without careful exclusion of air contact, it must be expected that even in sputter equilibrium contributions of titanium dioxide (formed by surface oxidation of the individual grains) and its reduction products (formed by preferential sputtering) are still present due to the inclusion of titanium dioxide within the pellet. These contributions may affect the spectra recorded by XPS and AES, respectively (9).

Fig. 2 shows AES spectra of the four reference materials. The spectra were recorded under continuous ion bombardment and after sputter equilibrium had been reached. It is clear that the spectra do not correspond to those of the pure oxides TiO_2, Ti_2O_3, and TiO, respectively, but represent only the result of a convolution of several effects. However, the spectra are characteristic of the chemical (and eventually the physical) state of the starting materials and of the treatment before measurement of the AES spectra. In addition, effects of the electron beam (6 c) as well as of instrumental parameters of the electron energy analyzer have to be regarded as further parameters, which may influence the shapes of the Auger spectra. It is, therefore, necessary to state that the experimental conditions have been kept constant during the acquisition of all spectra.

For the quantitative evaluation it has been assumed that the intensity ratio (termed Q) of the O(KLL) and the Ti ($L_3 M_{23} M_{23}$) transitions is proportional to the stoichiometric ratio in each reference material. The intensity of each Auger peak has been taken to be the peak-to-peak height without consideration of the course of the background and of any fine structure of the transitions. The Ti ($L_3 M_{23} V$) transition has been deliberately not used since the excitation probability of this transition varies significantly with the chemical environment (5,6 c) due to the participation of the valence band.
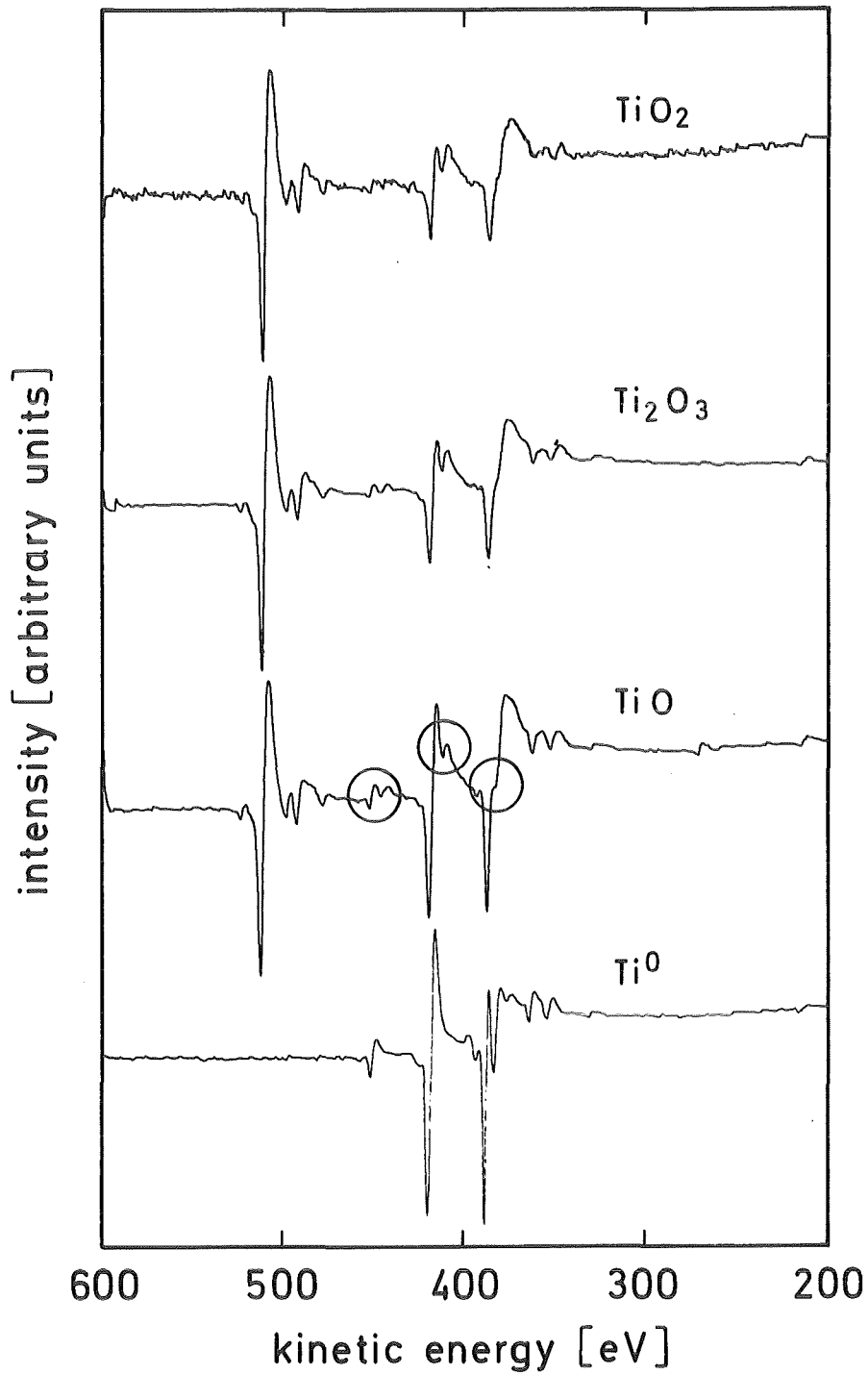
Fig. 2   AES spectra of TiO_2, Ti_2O_3, TiO, and Ti-metal. The oxide spectra are recorded under continuous ion bombardment after sputter equilibrium had been reached (indicated by constant peak intensities with further sputtering), the metal spectrum has been recorded after cleaning the surface by sputtering. The assignment of the major Auger transitions is as follows:

O(KLL): 515 eV kinetic energy; $Ti(L_3M_{23}V)$: 420 eV kinetic energy; $Ti(L_3M_{23}M_{23})$: 385 eV kinetic energy).

Fig. 3 shows the intensity ratios determined for the various oxides. The square data points correspond to the surface states of the oxides before sputtering, which have been shown by XPS to be titanium dioxide in all three cases. Those data points have, therefore, been entered at a stoichiometric ratio of two. The dashed line reflects the expected slope in case of a linear dependence of Q on the stoichiometric ratio.
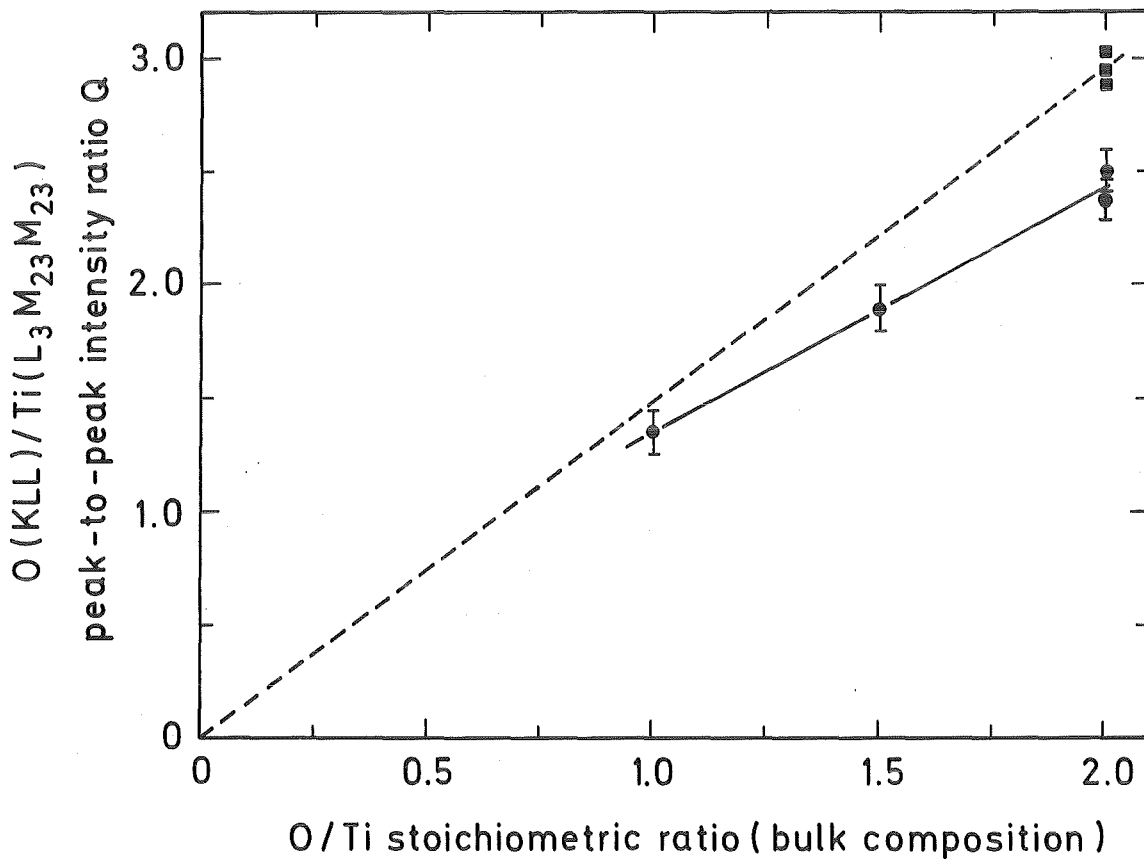

Fig. 3   Intensity ratio Q as a function of the bulk composition of the reference materials. The dashed line represents an interpolation between unsputtered titanium dioxide and zero. The full line connects the data points obtained from the reference samples in sputter equilibrium.

The full circles give the Q values of the oxides in sputter equilibrium, and the full line corresponds to the least squares fit of the data points. It is remarkable that the variation of Q can be well represented by a straight line with nearly no deviations. It is further remarkable that the value of Q of titanium monoxide almost coincides with the value expected from an interpolation between zero and the values of unsputtered titanium dioxide but that the deviation increases with increasing stoichiometric ratio of the bulk composition. This can easily be explained by preferential sputtering of oxygen because it can be expected that for a higher oxygen content in the unsputtered sample the percentage of sputter-reduced lower oxides is also higher.

Other authors have used the same approach for a quantification of titanium oxides (3 c,6 c). The results of these investigations are summarized in Fig. 4 and, together with our own measurements, in Table 1. Both groups observe a linear relation between the intensity ratio Q and the oxidation stage of the reference materials. This confirms that the empirical approach is a reasonable one. The slopes of the three fitted lines (Fig. 3,4) are slightly different. In our data and in the results of Mathieu et al. (6 c) the straight line does not pass through zero, while in the case of Gandon's results (3 c) it does very well. This may be an indication for the absence of preferential sputtering effects in Gandon's investigation. However, we believe that the observed differences lie within the error limits of the three investigations. It is rather astonishing that, remembering the various influencing factors on the surface composition of the samples (electron and ion beam effects, sample preparation etc.), the results of the investigations agree so well.

Additional information, especially on the chemical species present at the sample surface, can be obtained from a careful inspection of the Auger spectra of the standards. In Fig. 2 three regions are encircled marking details of the Auger spectrum, which vary significantly with the oxidation stage of titanium. The most drastic effect is observed when going from the oxidic phases to the metal. Due to these variations in spectral shapes it should , in principle, be possible to evaluate the chemical species, which contribute to the composition of a sample, from a combined interpretation of details of spectral features and of the observed intensity ratio Q.
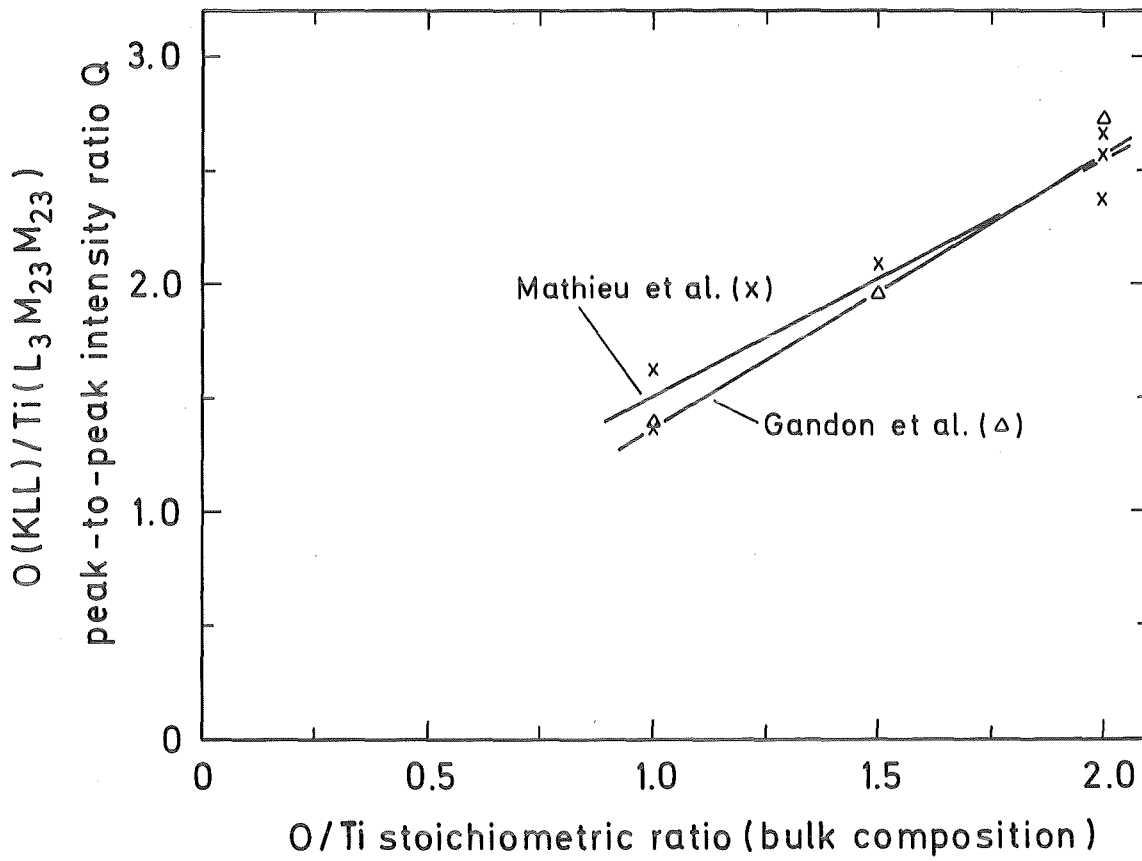
Fig. 4   Intensity ratio Q as a function of the bulk composition; values taken from literature (3 c, 6 c). Different results of one author for a specific oxide represent different sample preparation methods (cf. Tab. 1).

Table 1: Peak-to-peak intensity ratios Q of the O(KLL) and Ti($L_3M_{23}M_{23}$) Auger transitions from different authors determined for various titanium oxides prepared by different methods

sample preparation	Ref.	Q (determined in sputter equilibrium)		
		TiO	Ti_2O_3	TiO_2
pellet pressed from powder	6c[a]	1.62	2.08	2.56
	3c	1.38 ± 0.02	1.95 ± 0.03	-
	this work	1.36 ± 0.10	1.88 ± 0.10	-
vapour deposition	6c[a]	1.36	-	2.36
	3c	-	-	-
	this work	-	-	2.38 ± 0.10
				2.50 ± 0.10
anodic oxidation	6c[a]	-	-	2.66
	3c	-	-	2.71 ± 0.07
	this work	-	-	-

[a] Values taken from Fig. 3 in Ref. 6 c

3.   Interpretation of the effect of chemical oxidation on the Ti/Cu sample

Fig. 1 b shows, as already described in Chap. III.1, the depth profile of the oxidized Ti/Cu sample. The composition in the profile region with constant oxygen content can be determined using the peak-to-peak intensities for calculation of the value of Q. Fig. 3 then permits the calculation of the average stoichiometry. The relevant curve in Fig. 3 is the one, which is derived from the oxide reference samples in sputter equilibrium since the value of Q being characteristic for the composition of the Ti/Cu sample has also been derived during depth profile measurement. The evaluation is illustrated in Fig. 5. The result indicates a stoichiometry close to that of titanium monoxide.
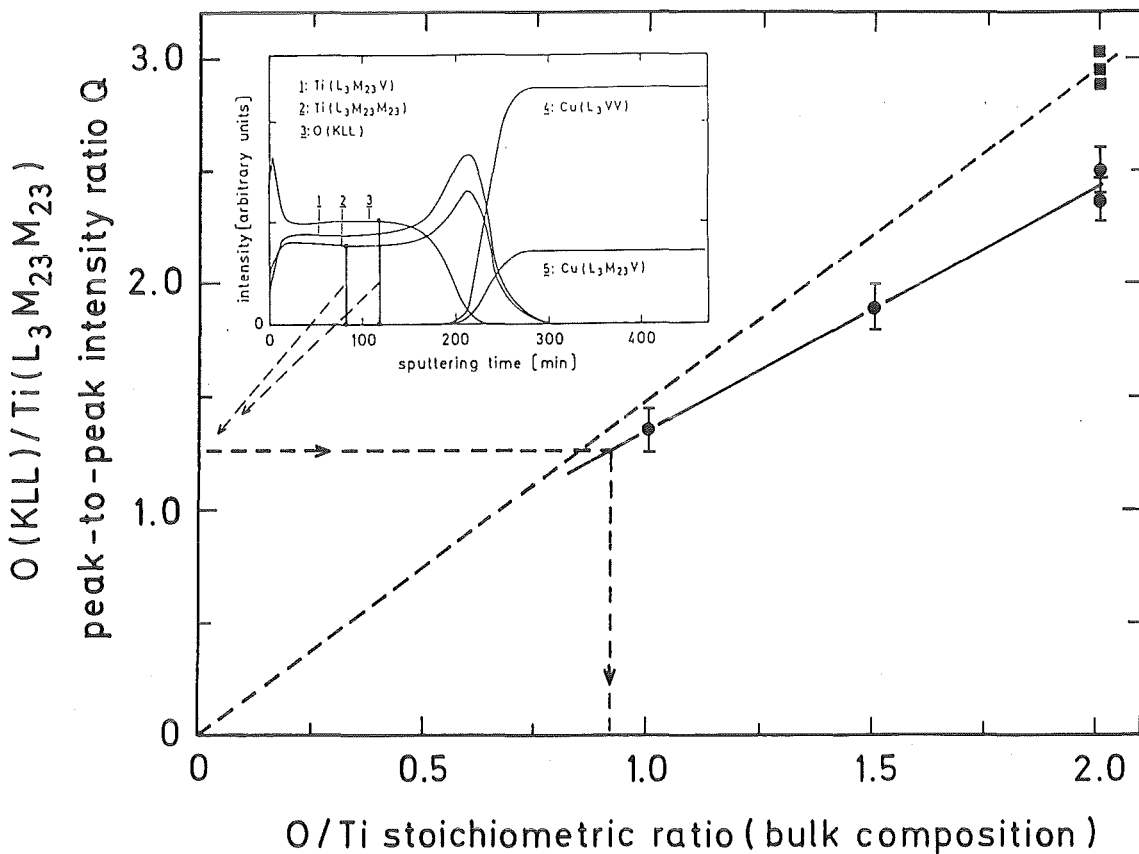

Fig. 5   Determination of the composition of the oxidized overlayer of the titanium/copper sample based on the evaluation of the spectra of the reference oxides. For an explanation of the curves compare Fig. 3. The inset (taken from Fig. 1 b) shows, for illustration, the depth profile of the sample from which the intensities of the Auger lines have been taken.
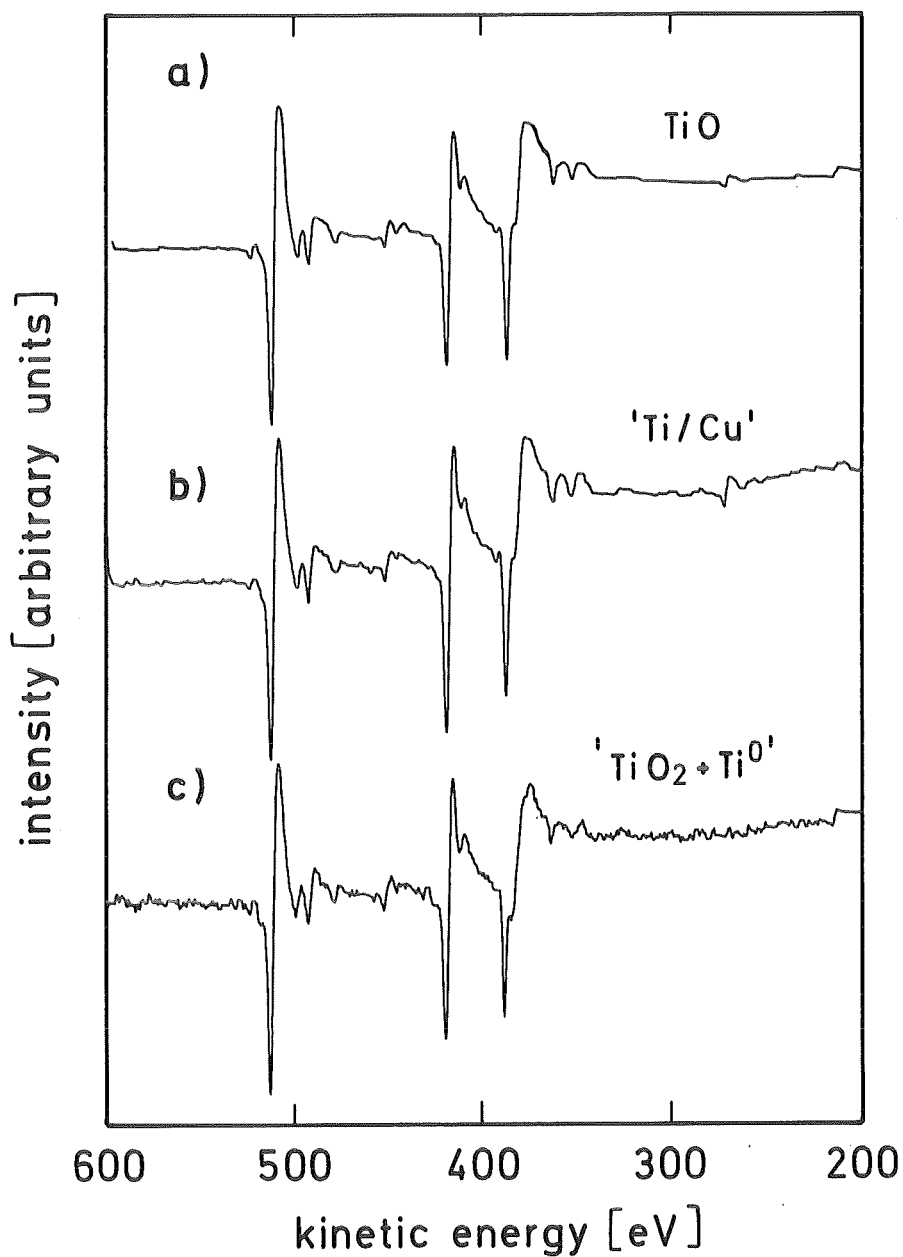
Fig. 6   Auger spectra of titanium monoxide (in sputter equilibrium) and of the titanium overlayer on copper (after removal of about half of the overlayer by sputtering, compare Fig. 1 b). The lower spectrum results from the summation of the Auger spectra of titanium metal and titanium dioxide in sputter equilibrium. The intensities of the two spectra were about equal with regard to the intensity of the Ti ($L_3M_{23}M_{23}$) transition.

When comparing the AES spectra from the plateau region of the profile with those of titanium monoxide in sputter equilibrium (Fig. 6 a and 6 b) one observes no significant differences even in those parts of the spectrum which vary characteristically with oxidation stage (compare Fig. 2). A simple straight-forward interpretation based on the experimentally determined stoichiometric ratio and the peak shapes could, therefore, lead to the conclusion that TiO has been formed over the major part of the overlayer and that the substrate is covered homogeneously with this oxide.

However, as discussed previously, the presence of open grain boundaries and the variation of the peak intensities of oxygen and titanium close to the Ti/Cu interface indicate the possibility of an oxidation at the grain boundaries leading to a heterogeneously distributed oxidation product (supposedly titanium dioxide). It can easily be shown that the Auger spectrum in Fig. 6 b is not only very similar to that of TiO but that it can be equally well reproduced by the summation of Auger spectra of titanium metal and titanium dioxide (in sputter equilibrium) of appropriate relative intensities. Fig. 6 c shows the result of such an attempt. The intensities of the contributing spectra are in this case approximately equal with regard to the intensity of the Ti (L_3 M_{23} M_{23}) Auger transitions in titanium metal and titanium dioxide, respectively. Obviously the ratio Q as well as the peak shapes of the sample spectrum are well reproduced by this method.

Therefore, the experimental observations can also be explained by the presence of titanium dioxide and titanium metal phases one beside each other. Auger electron spectroscopy is, in the present case, not suited to allow a conclusive distinction between the two possible oxidation mechanisms. Additional information is necessary, which can be obtained e.g. from XPS measurements, which in many cases are more sensitive and conclusive to different chemical species.

Fig. 7 a shows the Ti 2p XPS spectra of the Ti/Cu sample after sputtering until the plateau region of the profile (Fig. 1 b) had been reached. For comparison Fig. 7 b shows the XPS spectrum of titanium metal. The binding energies of the Ti 2p photopeaks of the upper spectrum are very close to the values of the metal and are definitely different from those of titanium monoxide, which are shifted by about 1.5 eV to higher binding energies (2,8). Differences between the two spectra are indicated by the hatched area in Fig. 7 a. These differences correspond to contributions of titanium oxides (for a detailed evaluation compare Ref. 12). These observations show that, indeed, the mechanism, which is based on an oxidative attack of the peroxide solution at the open grain boundaries, must be the relevant

one. On the other hand, the AES measurements are suited only for the determination of the integral composition of the surface analyzed. It can be estimated from these results that titanium metal and titanium oxide cover about one half of the analyzed surface each (12).
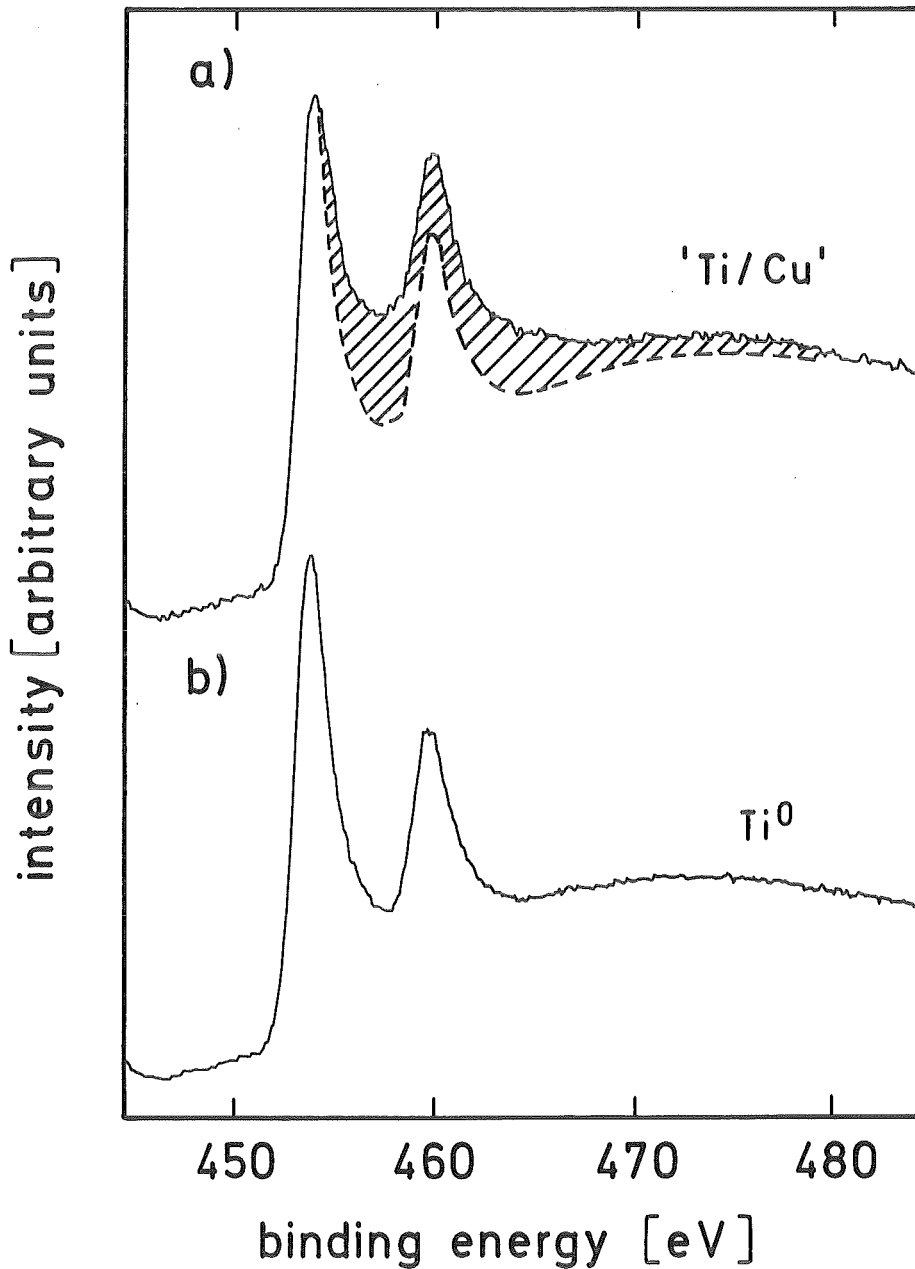

Fig. 7 (a) Ti 2p XPS spectrum of the titanium/copper sample after sputtering until the plateau region of the overlayer (compare Fig. 1 b) had been reached; (b) Ti 2p XPS spectrum of pure titanium metal. The hatched area in the upper spectrum indicates a contribution of oxidic components.

IV. Conclusions

It has been shown that Auger spectra have to be evaluated very carefully if one is interested not only in the average composition of the sample but also in a chemical speciation. In the case of partially oxidized titanium the Auger spectra cannot be interpreted unambiguously, even if details of the spectral features are additionally taken into consideration. This is of course only true if the characteristic dimensions of the heterogeneity are much smaller than those of the surface area analyzed by AES. However, a reduction of the probed area is only helpful if one can get access to homogeneously composed sample volumes. In other words, the dimensions of the heterogeneity have to be known and, in addition, one must be able to localize differently composed parts of the sample, which is only possible with an appropriate instrumentation. This means that in the case of "unknown" samples, there remains some uncertainty about the interpretation of the results.

In view of these limitations the determination of AES transition intensity ratios only provides an average composition of the analyzed surface area and can only be converted to a chemical speciation if additional information is available from a supplementary technique like e.g. XPS. Nevertheless, determination of intensity ratios can provide useful supplementary information, especially since it has been shown that the evaluation procedure can be applied, at least in the case of titanium oxides, to reference materials of different preparation processes and measured under varying experimental conditions.

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