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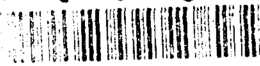

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RSRE MEMORANDUM No. 4281

ROYAL SIGNALS & RADAR ESTABLISHMENT

A STUDY OF COPPER SEGREGATION IN SPUTTERED Al-Si-Cu FILMS USING AUGER ELECTRON SPECTROSCOPY

Authors: M A Green & D C Rodway

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ROYAL SIGNALS AND RADAR ESTABLISHMENT

Memorandum 4281

TITLE: A STUDY OF COPPER SEGREGATION IN SPUTTERED AL-SI-CU FILMS USING AUGER ELECTRON SPECTROSCOPY.

AUTHORS: M.A.GREEN and D.C.RODWAY

DATE: JANUARY 1991

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SUMMARY

A study has been made, using Auger Electron Spectroscopy (AES), of copper copper segregation in Aluminium-Silicon-Copper films processed in the Silicon Processing and Evaluation Laboratory (SPEL).The AES technique and its' interpretation are briefly discussed. A description of the Auger Spectrometer and experimental details are also provided.

The effects of variations in layer thickness and annealing temperatures on the interface between the Al-Si-Cu and the silicon substrate were studied. Results obtained from other samples from British Telecom research laboratories, and alternative analysis methods such as Rutherford Backscattering (RBS) are also discussed and conclusions drawn as to the nature of this segregation.

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A STUDY OF COPPER SEGREGATION IN SPUTTERED AL-SI-CU FILMS USING AUGER ELECTRON SPECTROSCOPY (AES)

Mrs.M.A.Green & Dr.D.C.Rodway

Introduction

Al-Si-Cu alloy has been widely used for metal interconnects in integrated circuits, largely to improve electromigration and surface topography. However there have been problems with the technique of Reactive-Ion-Etching (RIE) used to pattern these interconnects, since copper has no volatile halides and does not combine easily with the reactive gases used in the dry-etching process.This has meant that the removal of copper becomes difficult, unless the ion energies used in the process are sufficient to remove them by physical sputtering.

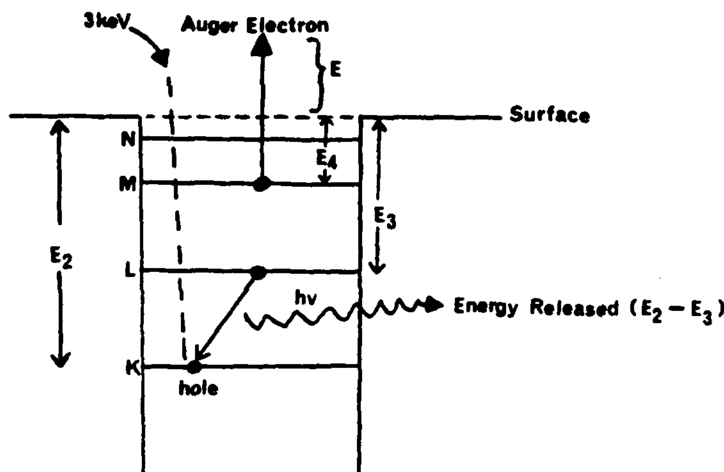
Recently it became apparent that some of the problems experienced by the "Silicon Processing and Evaluation Laboratory" (SPEL) in etching these alloys might be attributable to the presence of copper residues, resulting from either a non-uniform distribution of copper within the bulk of the sputtered Al-Si-Cu layer, or possibly a build-up of copper at the critical "Oxide- Metal" interface, as a result of the etching process.

The work undertaken here is a study, using depth profiling Auger Electron Spectroscopy (AES),of the copper distribution in R.S.R.E. sputtered Al-Si-Cu with the objective of facilitating its dry-etching.

The AES Technique

Auger electron spectroscopy was used for this particular study, since it's combination of high surface sensitivity and good spatial resolution made this the most suitable type of analysis. AES is a method of studying the composition of the outer 1-5 atomic layers of the surface of a solid, without destroying the surface itself.
Auger Electrons are produced by bombarding the specimen surface with electrons of energies from 1-10keV. Some of the electrons within the surface atoms of the sample are excited which then results in an electron re-arrangement within the the atom.

Typical energy transitions that can occur are shown here.



Here,an electron from the K energy level is ejected by the incident electron and an electron from the L level fills the vacant site. The energy released is transferred to a third electron,either in this atom or an adjacent atom, and this third electron is then ejected as an Auger electron.

The Auger electrons energy is given by :- $E \sim (E_2 - E_3) - E_4$ (see above)

As E_2, E_3, E_4 are characteristic of the electronic structure of the particular element concerned, it is possible to determine the chemical composition of the sample surface by measuring both the energies and number of Auger electrons.

AES is a non-destructive technique, in that the surface itself is not eroded and normally it's nature is unchanged.

The energies of the Auger electrons are low, typically 20 - 2000 eV, so that although they may be produced from as far within the solid as the original electron beam penetrates, only those generated from the first two or three atomic layers below the surface will escape with their original energies intact.
Any Auger electrons which originate further within the sample lose energy in inelastic collisions and cannot be identified. Hence, the technique gives great surface sensitivity, and can detect as little as 0.1% of a monolayer of impurity in the surface. Only Hydrogen and Helium cannot be detected since these elements do not possess sufficient elecron shells for the Auger Transition to occur.

The Auger features in the electron energy distribution are comparatively small in amplitude, and occur on a large sloping background of secondary electrons which makes their detection difficult.This secondary electron background originates from incident electrons scattered within the sample, electrons that have been directly ejected from the sample atoms by the electron beam and Auger electrons that have been scattered within the sample.

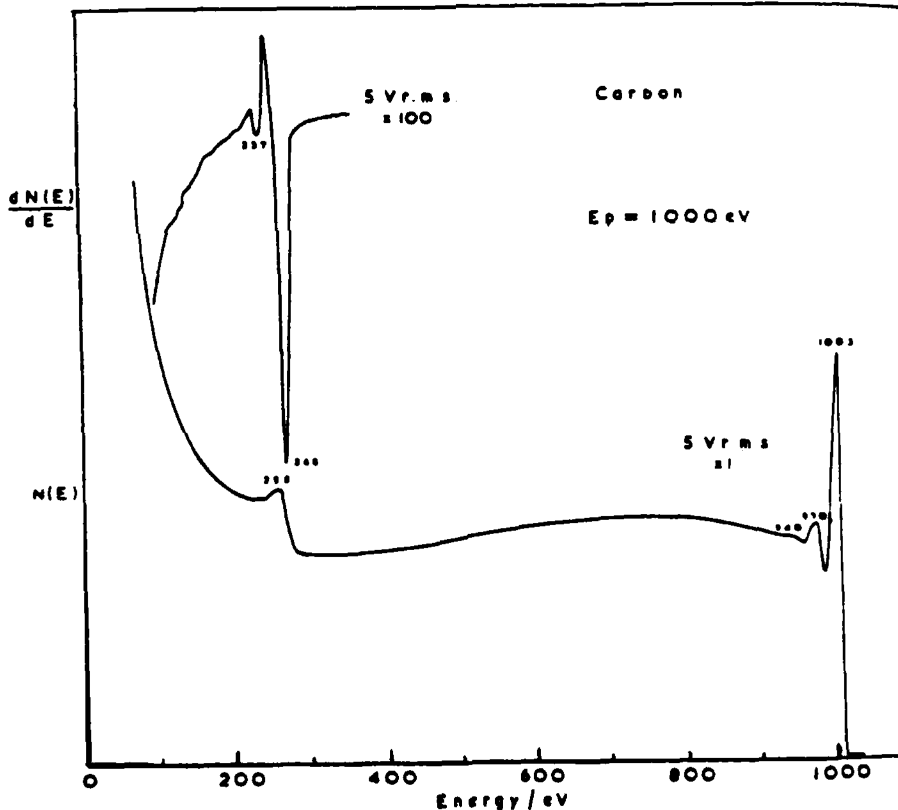
Consequently, spectra are usually differentiated with respect to energy

so that, $\frac{dN(E)}{dE}$ vs E is displayed.

This suppresses the background and accentuates the prominence of the Auger peak. Quantification of the results is achieved using published elemental sensitivity factors and formulae.

Interpretation of the Auger Spectra

The figure below shows a typical Auger spectrum in the $\frac{dN(E)}{dE}$ and N(E) forms for carbon.



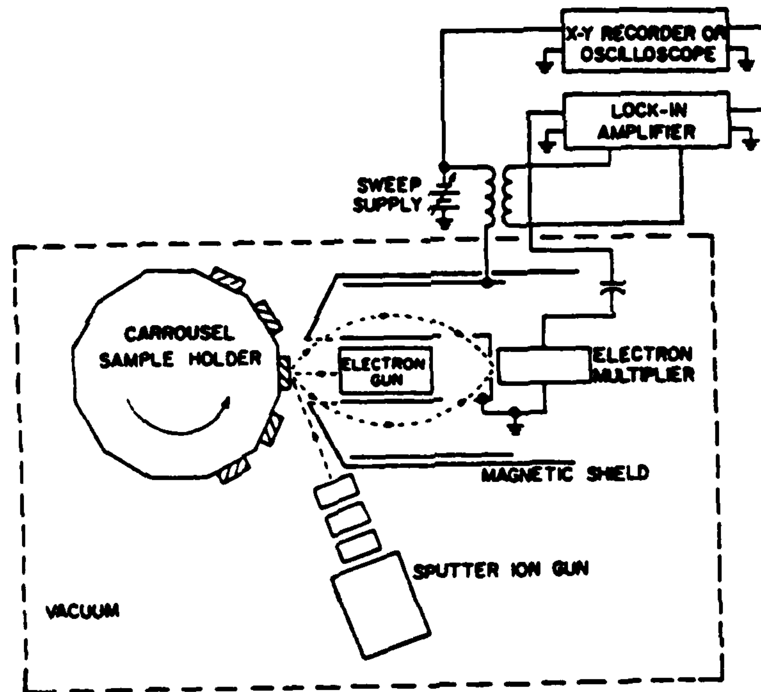
Lower curve:- energy distribution N(E) of back-scattered electrons from a carbon surface at energy 1000eV.

Upper curve:- portion of the differentiated distribution dN(E)/dE, demonstating the improved resolution of Auger features gained by differentiating with respect to energy.

Conventionally, the energy of the Auger peak is taken to be the energy corresponding to the smallest negative part of the Auger transition, since it is usually the sharpest and most prominent. The peaks at high electron energy result from reflection of the incident beam and loss peaks associated with this reflection. In most elements a number of Auger transitions occur, hence different elements can be identified by the presence of characteristic peaks at well defined energies.

The Auger Spectrometer

The general layout of a typical Auger Electron Spectrometer is shown below. Essentially, it consists of a vacuum chamber with an electron gun which produces an electron beam of 1-10 KeV. Also within the chamber is an electron spectrometer which analyses the energies of the emitted electrons.An ion gun is also included for cleaning the surface of the specimen, and for composition depth profiling.



Samples are normally mounted onto a carousel holder which is attached to a manipulator for accurate sample positioning. The technique must be carried out under Ultra High Vacuum since, at higher pressures,residual gas atoms are adsorbed on the sample surface. For example, at a pressure of 10^{-6} Torr, a monolayer will be deposited onto a clean surface in approximately one second, which would give insufficient time for analysis . So pressures < 10^{-10} Torr are necessary.

Experimental details

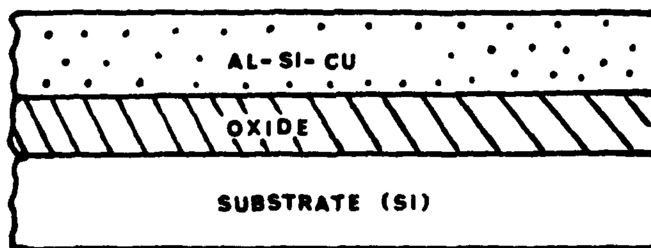
The Auger spectrometer used for this work was a Varian 10kV Cylindrical Mirror analyser (CMA) fitted to a 12" diameter ion pumped ultra high vacuum (UHV) vessel with a base pressure of < 5×10^{-11} torr. This vessel was fitted with an airlock and samples could be inserted with a cycle time of approximately 30 minutes. The vessel was further fitted with two ion guns (Varian 3kV) positioned at opposite sides of the CMA so as to reduce ion beam induced topographical effects whilst depth profiling.(2) The standard Varian detection system was modified by the addition of a Nicolet 12/75 computerised signal averager for the recording, storage and manipulation of the Auger spectra.

The Varian CMA is capable of spatial resolution of ~ 5μm , but in order to reduce the possibility of electron beam induced effects on the sample, the beam was electronically rastered over an area of approximately 100μm square. Depth profiling of the layers was accomplished using 3kV Ar^+ ions and slow etch rates (~ 2000A/min). The sample under examination was covered by a molybdenum mask which exposed a 1mm diameter circle of the surface and the ion beams were rastered over a larger area (1cm x 1cm). This gave a well defined crater in the sample surface, the depth of which could be measured later using a Sloan Dektak 11A. Quantification of the results was carried out using published elemental sensitivity factors(5) and the formulae from Seah and Dench.(3)

Samples and preparation

The samples used in these analysis trials were bulk silicon wafers of typically 1-50 Ωcm, "N" type. These wafers were thoroughly cleaned in a "Class 1000" atmosphere, before being inserted into an oxidation furnace at 900°C for 70 minutes, to grow a thermal oxide approximately 0.1 μm thick.

The schematic below shows the sandwich structure of the wafers studied:-

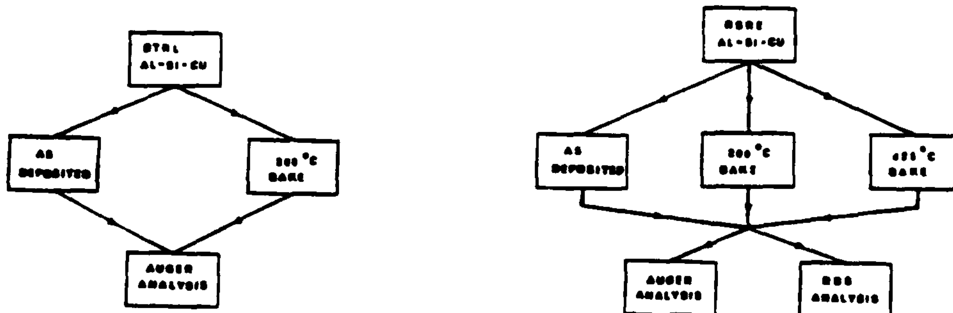


Once oxidised, the wafers were immediately transferred to a "CVC 601" sputtering chamber, pumped by a Cryo-pump to a base pressure of 9.8 x 10-8 torr. After a 2 minute flush in pure argon, and a 10 minute pre-sputter to achieve thermal equilibrium, the wafers were sputtered with a layer of Al-Si-Cu, at a pressure of 5 millitorr, from a solid target of nominal composition:

95% Aluminium: 1% Silicon: 4% Copper

The samples were then cooled " in-situ" in argon for 5-10 minutes.

Three thicknesses of metal were studied: 1.0 μm, 0.375 μm and 0.1 μm. These were studied at several stages as shown by the flow-chart below.



Here, the two anneals were carried out to simulate the conditions normally seen by a typical device wafer during processing:

The 200°C anneal is a dehydration bake before the "Photolithography" or patterning stage.

The 425°C anneal is the final "firing-in" of the wafer , used to lower contact resistance and promote adhesion between the metal interconnects and the under-lying material.

In order to provide a comparison for this study of Al-Si-Cu, some of the samples profiled by AES, were also analysed by Rutherford Backscattering (RBS) at the University of Birmingham. Two samples were also sent to British Telecom Research Laboratories(BTRL) for thermal oxide and Al-Si-Cu growth, in order to establish if the copper segregation was an R.S.R.E phenomenon. Both these samples were examined in the same way as the RSRE samples.

SUMMARY OF SAMPLES

SAMPLE No.	LAYER 1	LAYER 2	TREATMENT
AL39	RSRE Oxide	1μm Al-Si-Cu	As deposited
AL35	RSRE Oxide	1μm Al-Si-Cu	200°C Anneal
AL33	RSRE Oxide	1μm Al-Si-Cu	425°C Anneal
AL317-1	RSRE Oxide	1μm Al-Si-Cu	As deposited
AL317-2	RSRE Oxide	1μm Al-Si-Cu	200°C Anneal
AL376	RSRE Oxide	0.375μm Al-Si-Cu	As deposited
AL432	RSRE Oxide	0.1 μm Al-Si-Cu	As deposited
BTRL-1	BT Oxide	1μm Al-Si-Cu	As deposited
BTRL-2	BT Oxide	1μm Al-Si-Cu	200°C Anneal

Results

1) Standard Thickness layers (1.0μm)

a) As-deposited:

Al-Si-Cu samples of typically 1.0μm thick were initially examined by AES; it was found that these profiles all had a similar shape i.e. as the layer was profiled, the composition of the layer remained fairly constant for the first 9000A , following which there was a rise in the copper level as the Metal-Oxide interface was approached.
Since the target composition was nominally 4% Cu,the copper levels in the bulk of the material should have remained constant at 4% throughout the metal layer. Figures 4 and 5 show this rise in the copper level in more detail and it can be seen that the copper concentration rises from a level of approximately 1% in the bulk to a peak of 7% at the interface.
Several 1.0μm samples were studied in this way, and all were found to have this characteristic peak at the Metal-Oxide interface.

b) 200°C Anneal:

Corresponding samples were then given a 200°C anneal for 30 minutes and again analysed using AES. Here the 1 μm samples (Fig.6) and (Fig.7) all showed the same trend as before. This time, however, there was a greater depletion of the copper concentration in the bulk of the Al-Si-Cu layer and an increase in the height and width of the copper peak at the interface. The copper level in the bulk of the layer was now typically 0.5% rising to a peak of 7-10% at the interface with a peak width (measured at full width, half maximum) of 1820 A (Fig.9). Although there was variation between individual depositions, where there were unannealed and annealed samples from the same deposition, the rise in the copper peak and the broadening of the peak were always seen.

c) 425°C Anneal:

This anneal resulted in an exaggeration of the effect seen in the 200°C anneal (Fig.8). Here there was almost total depletion of the copper levels in the bulk and a further broadening of the peak at the interface.

i) With AL39 , the as-deposited sample , there was approximately 1% copper in the bulk of the layer which rose up to 7.5% at the metal-oxide interface. In this sample the peak width was approximately 1770A.

ii) Sample AL35, had been annealed at 200°C , and here the level of copper in the bulk of the layer dropped to approximately 0.5% rising to ~ 7% at the interface. The peak width was approximately 1820A but here the amount of copper in the bulk level was slightly less,which suggested a re-arrangement of copper had taken place.

iii) This effect was more noticeable with the last sample AL33 , which had been annealed at 425°C. The level of copper found in the layers before the interface had now virtually disappeared and the peak width was broadened to approximately 2300A, at a level of about 7% , which again showed this migration of copper from the bulk of the layer to the interface.

2) Effect of Thickness Variation

In order to establish that this effect was not thickness dependent samples of 0.375μm and 0.1μm thickness were studied. This also served to ensure that the peak was not target dependant i.e. if the target itself had been copper rich at the surface then it would have been reasonable to expect a build-up of copper at the interface , since this would be the first point of contact of the sputtered material. By looking at very thin layers , any target enrichment would be apparent by a high level of copper throughout the bulk of the thinner layer.

In fact , samples of 0.375μm and 0.1μm showed the same characteristic Copper spectra as their thicker counterparts .(Fig.10, Fig.11) As would be expected of a thinner sample , the peak was proportionally smaller than in the thicker samples i.e. 4% as opposed to ~ 7%, but had the same interface "peak" as before.

3) British Telecom Samples

This particular study was hampered by an apparent difference in the underlying thermal oxide. The British Telecom (BT) samples were profiled in exactly the same manner as the R.S.R.E samples , but exhibited significant "charging" effects during analysis.These effects distorted both the shape and position of the copper peak causing significant gaps in the data. (Fig.12-15)

Nonetheless it was still possible to see the same trend at the interface as with the other samples although it was not possible to measure the copper percentage accurately.

4) Other Analysis Techniques

i) R.B.S.

Some of the layers examined by AES were also examined by Rutherford Backscattering (RBS). In RBS energetic beams (0.5 - 3.0 MeV) of light ions (H^+ D^+ He^+) impinge on a target and a small proportion of the ions undergo collisions with the nuclei of the target atoms. Measurement of the energy of the scattered particles gives the mass of the target atom.This method can provide information on the depth distribution of elements in a sample without the need for stripping by ion erosion and is a quantitative method accurate to approximately 5%. The RBS technique depends on the fitting of a scattering model to the results and gives a histogram plot rather than a continuous measure of copper concentration.

Figures 16 ,17 and 18, compare the two techniques using the 1μm samples at their three stages of anneal , plotted on the same graph. Qualitatively the agreement is excellent , although the quantitative agreement is less good, possibly due to the model fitting necessary with RBS.

5) Analysis of the Sputtering Target

Since there appeared to be a discrepancy between the nominal target percentage of copper (95% AL- 4% Cu - 1% Si),and that found in the bulk of the layers examined , an Auger profile was taken from a section of the sputtering target used for the deposition of these layers.

For confirmation of the copper level found by AES , Energy Dispersive Analysis by X-Rays (EDAX) measurements were also made on the same sample. This technique has the additional benefit that it is possible to check the actual composition of the target (~ 1μm depth), in order to establish that the non-uniformity of copper found in the AES profile was not due to any specific surface enrichment of the target itself.

The results of both AES and EDAX indicated similar percentages of copper in the target material examined. AES showed a composition of 1.6% , whilst EDAX gave the composition to be 1.8%. This indicated that the levels of copper measured in the deposited layer using AES were essentially correct despite the difference from the nominal composition of the Al-Si-Cu target.

Conclusions

It was possible to draw certain conclusions from the AES study of these Al-Si-Cu layers :-

1. Problems associated with the "Reactive-Ion-Etching" of Al-Si-Cu can be linked to a build-up of copper at the critical Metal/Oxide interface.This non-uniformity in the copper distribution is not due to any non-uniformity of the sputtering target itself. However, the target composition does vary from the manufacturers specification.

2. There is a significant degree of migration of copper from the bulk of the layer to the interface , and this effect is temperature dependant; an anneal of the layer resulting in an increase in both the copper concentration and depth of the enriched layer , with subsequent depletion of the bulk layer.

3. Although this phenomenon was also apparent on those samples obtained from BTRL , significant differences between thermal oxides made evaluation difficult. Charging effects , normally associated with insulators , were not seen on the RSRE samples as might be expected . This may possibly be due to metal atoms being driven into the oxide some distance by the RSRE sputtering process, resulting in some conduction.
   However , further study beyond the scope of this report would be necessary to verify this.

Acknowledgements

The Authors would like to thank the members of the Silicon Processing and Evaluation Laboratory (SPEL) for the preparation of test samples. In particular , Mr P Branfield and Mr A Morpeth from the "Deposition" module , and Mr J Crabb from the "Etching" module. Thanks also go to Mrs D Dosser for her help with the EDAX measurements , and BTRL for providing comparison samples.

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LIST OF FIGURES

FIGURE 1......................1μm Al-Si-Cu Theoretical Depth Profile

FIGURE 2......................1μm Al-Si-Cu Depth Profile (AL39)

FIGURE 3......................1μm Al-Si-Cu Depth Profile (Al317-1)

FIGURE 4......................AL317-1 - Copper levels only

FIGURE 5......................AL39 Copper levels only

FIGURE 6...................... 1μm sample- 200°C anneal (AL35)

FIGURE 7......................1μm sample- 200°C anneal (AL317-2)

FIGURE 8......................1μm sample- 425°C anneal (AL33)

FIGURE 9......................AL35 Copper levels only

FIGURE 10.....................0.1μm sample - AL432 Copper levels

FIGURE 11.....................0.375μm sample - AL376 Copper levels

FIGURE 12.....................British Telecom sample-AES Profile(BTRL-1)

FIGURE 13.....................British Telecom sample-Cu levels (BTRL-1)

FIGURE 14.....................British Telecom sample-AES Profile(BTRL-2)

FIGURE 15.....................British Telecom sample- Cu levels (BTRL-2)

FIGURE 16....................."RBS" plotted on AL39 Copper profile

FIGURE 17....................."RBS" plotted on AL35 Copper profile

FIGURE 18....................."RBS" plotted on AL33 Copper profile

FIG.1

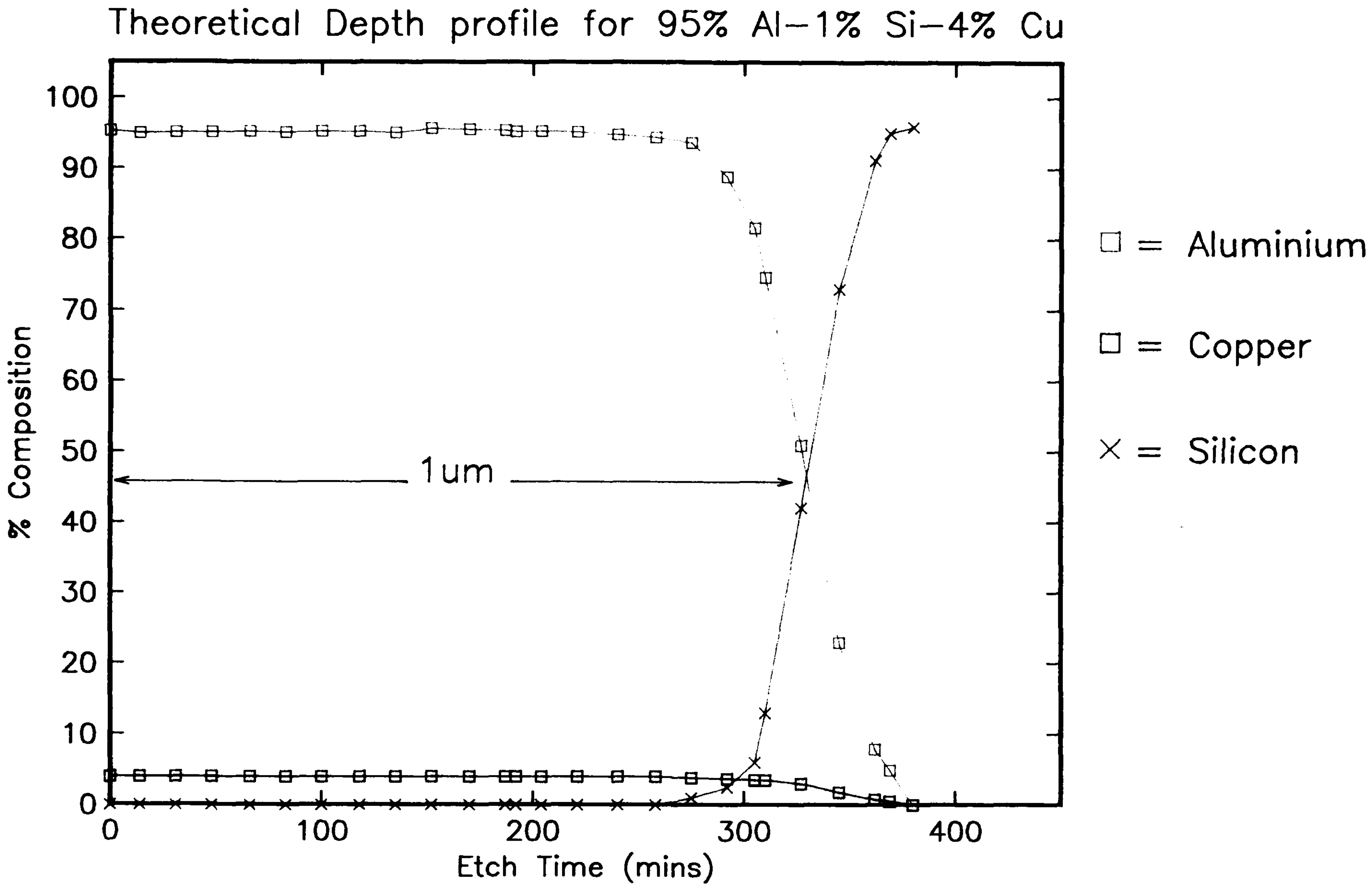


FIG.2

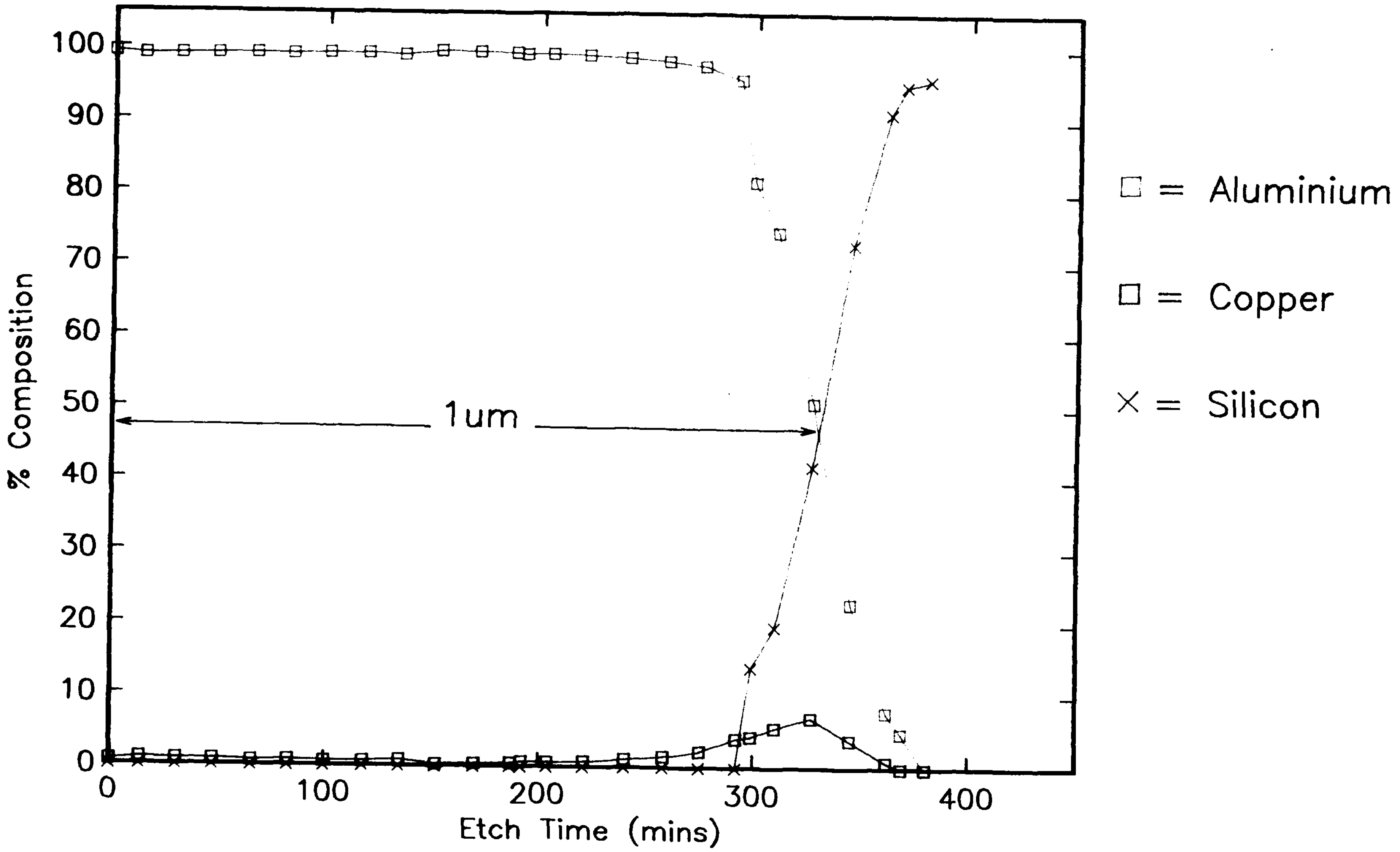


FIG.3

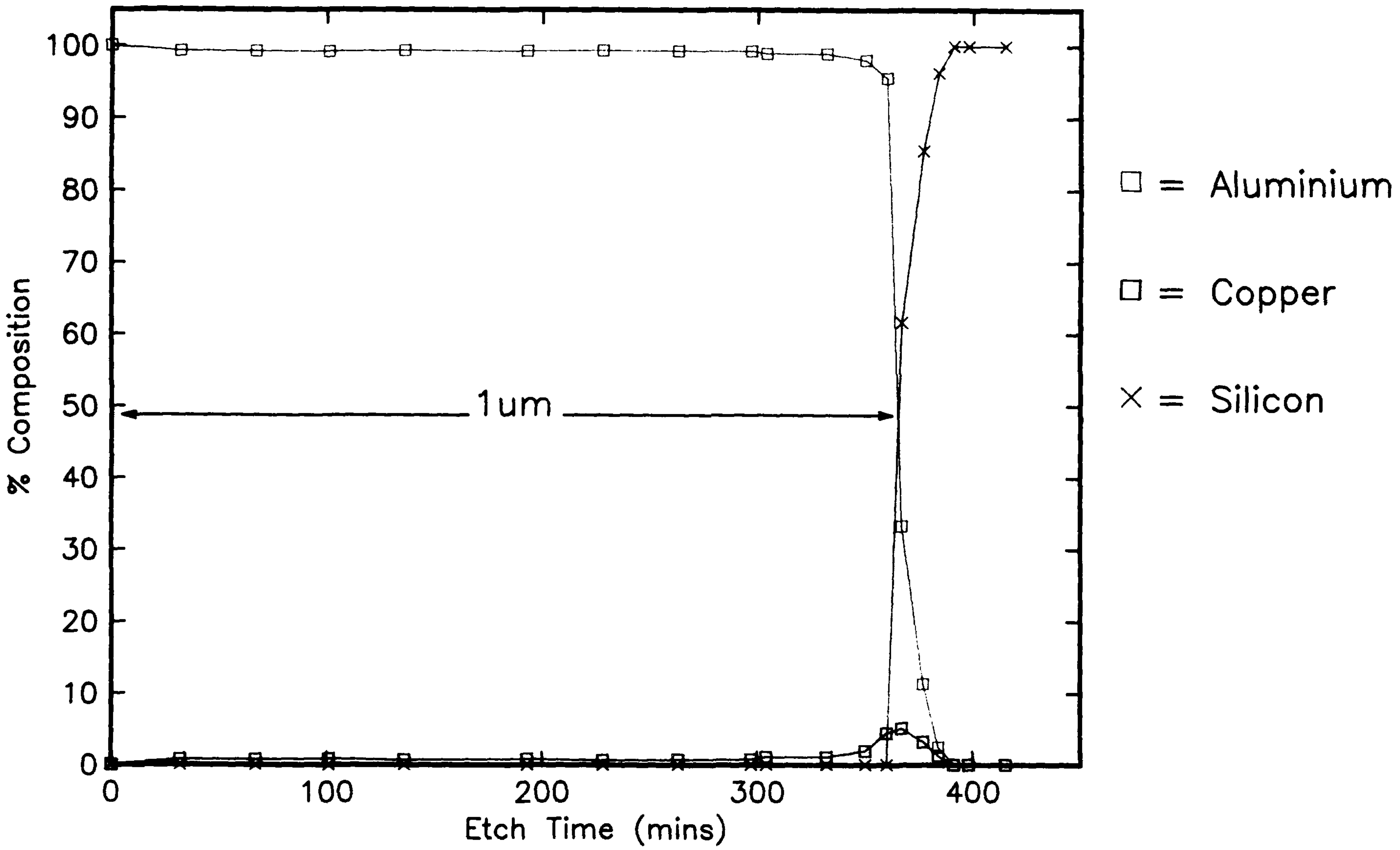


FIG.4

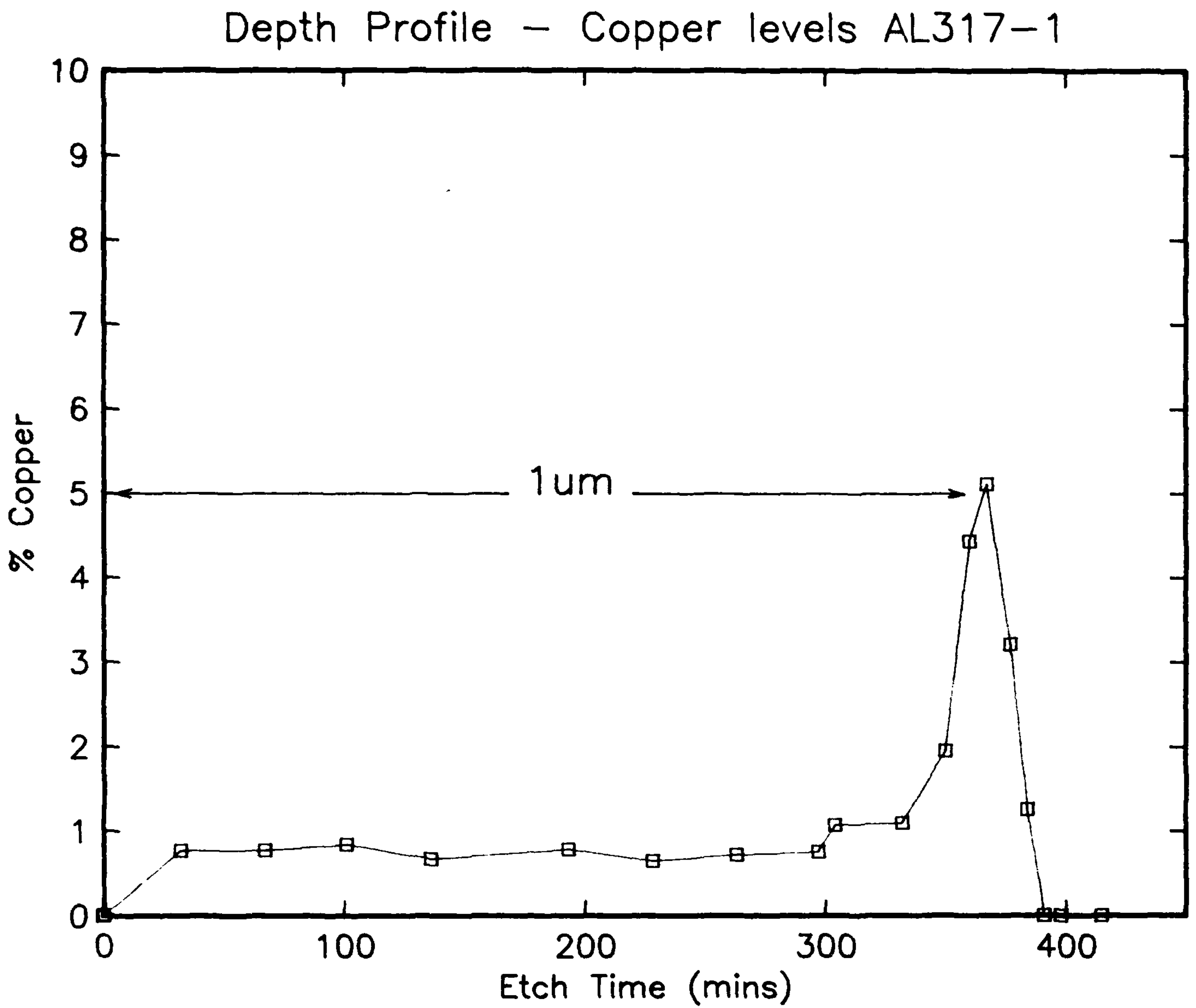


FIG.5

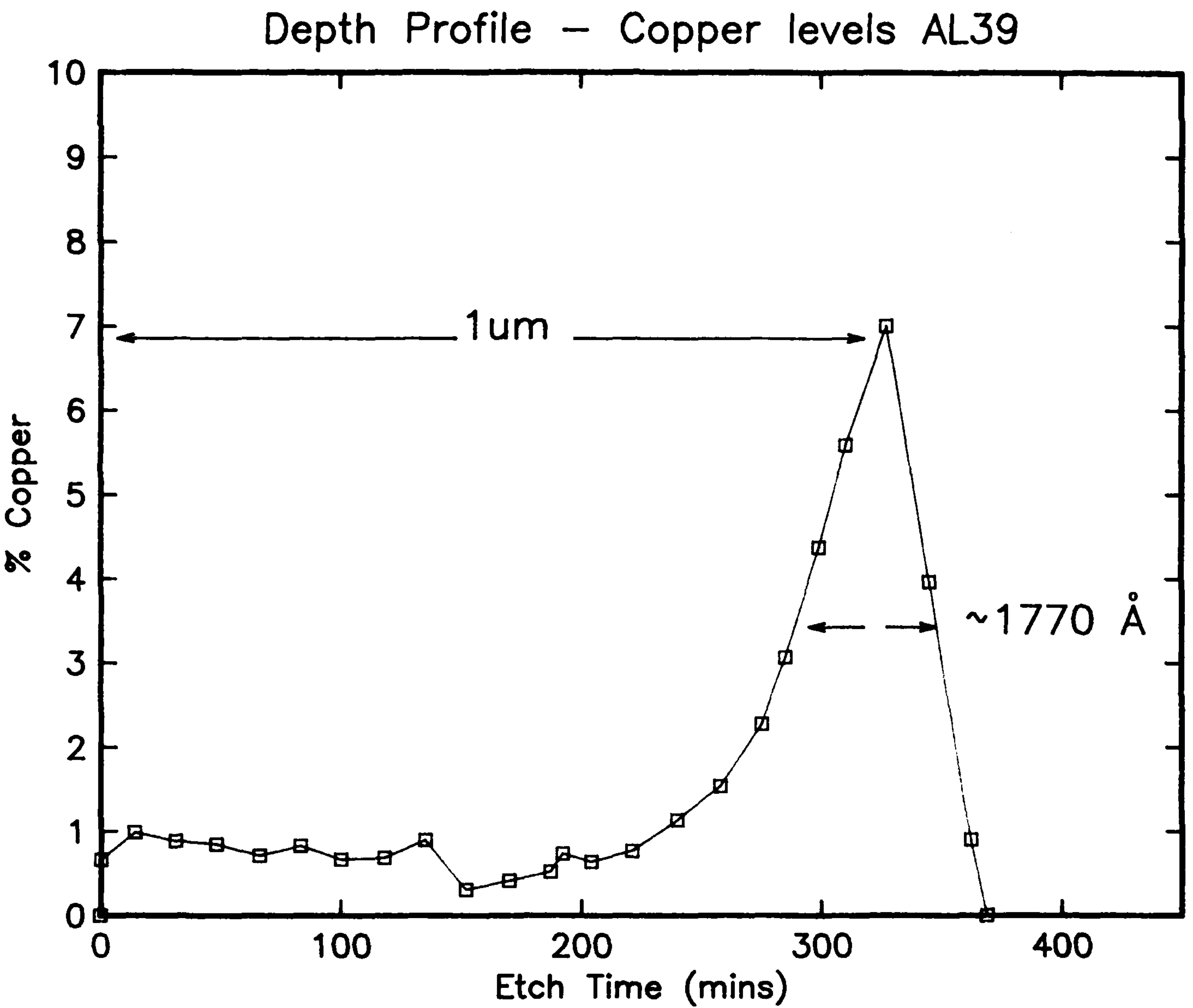


FIG.6

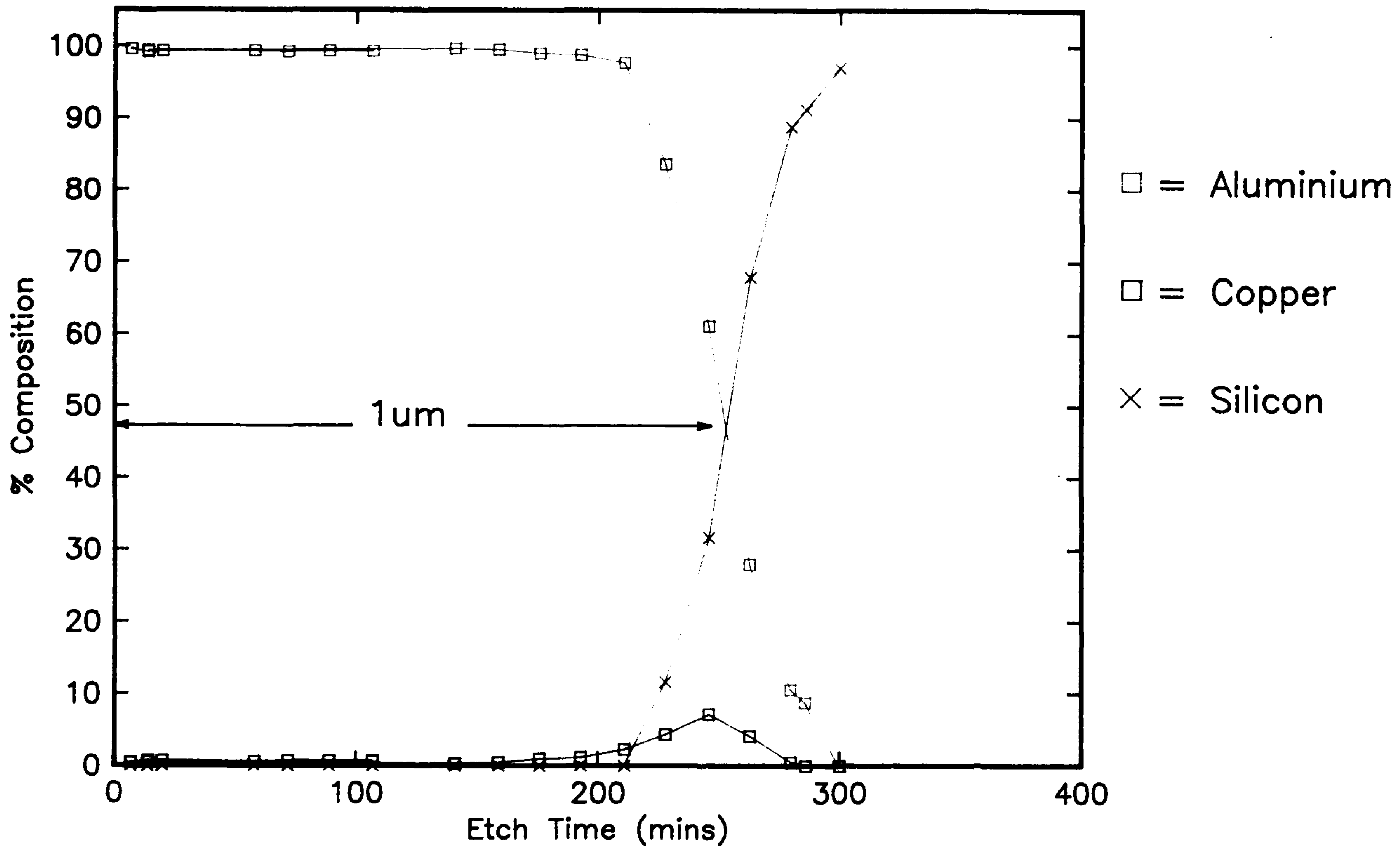


FIG.7

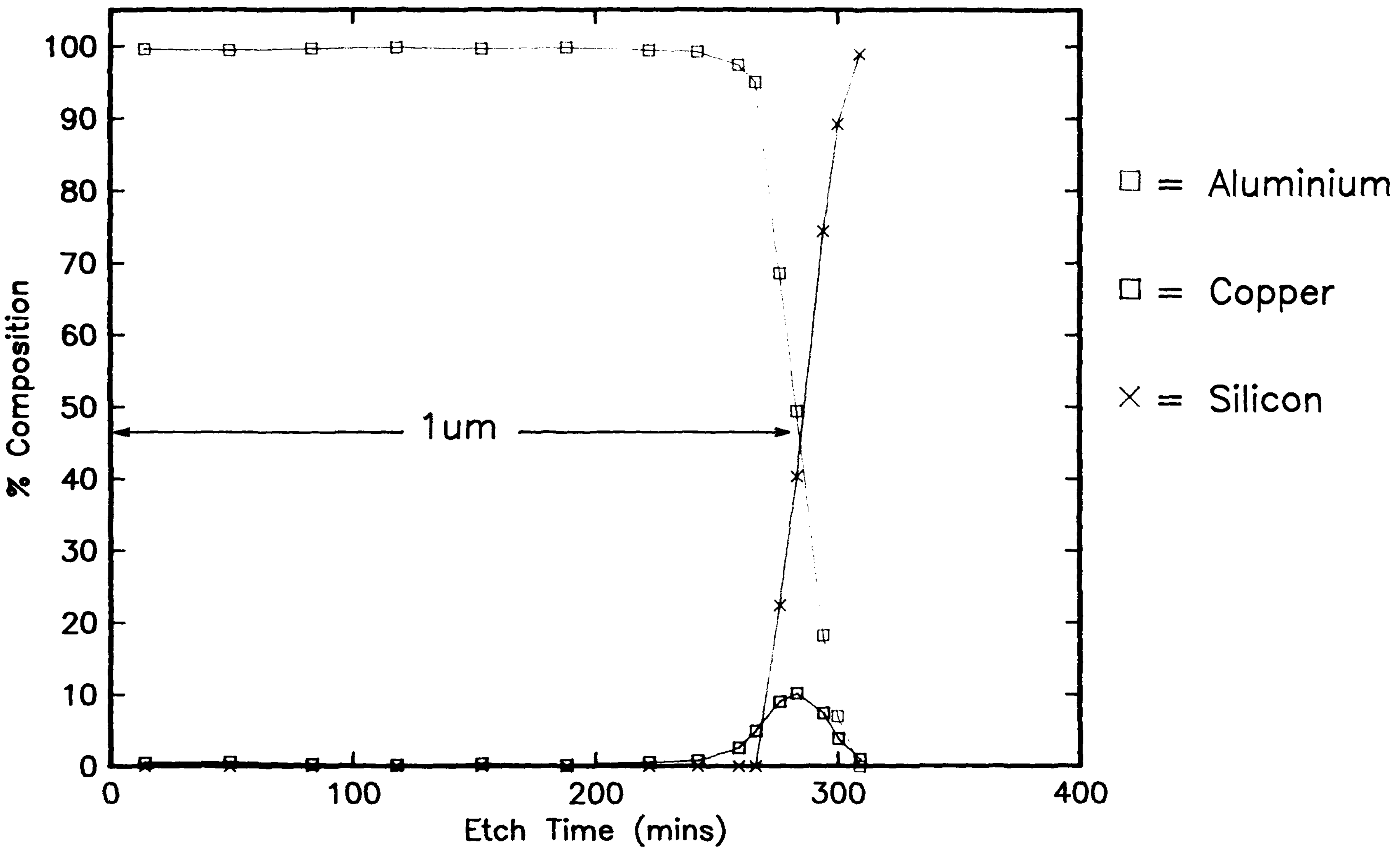


FIG.8

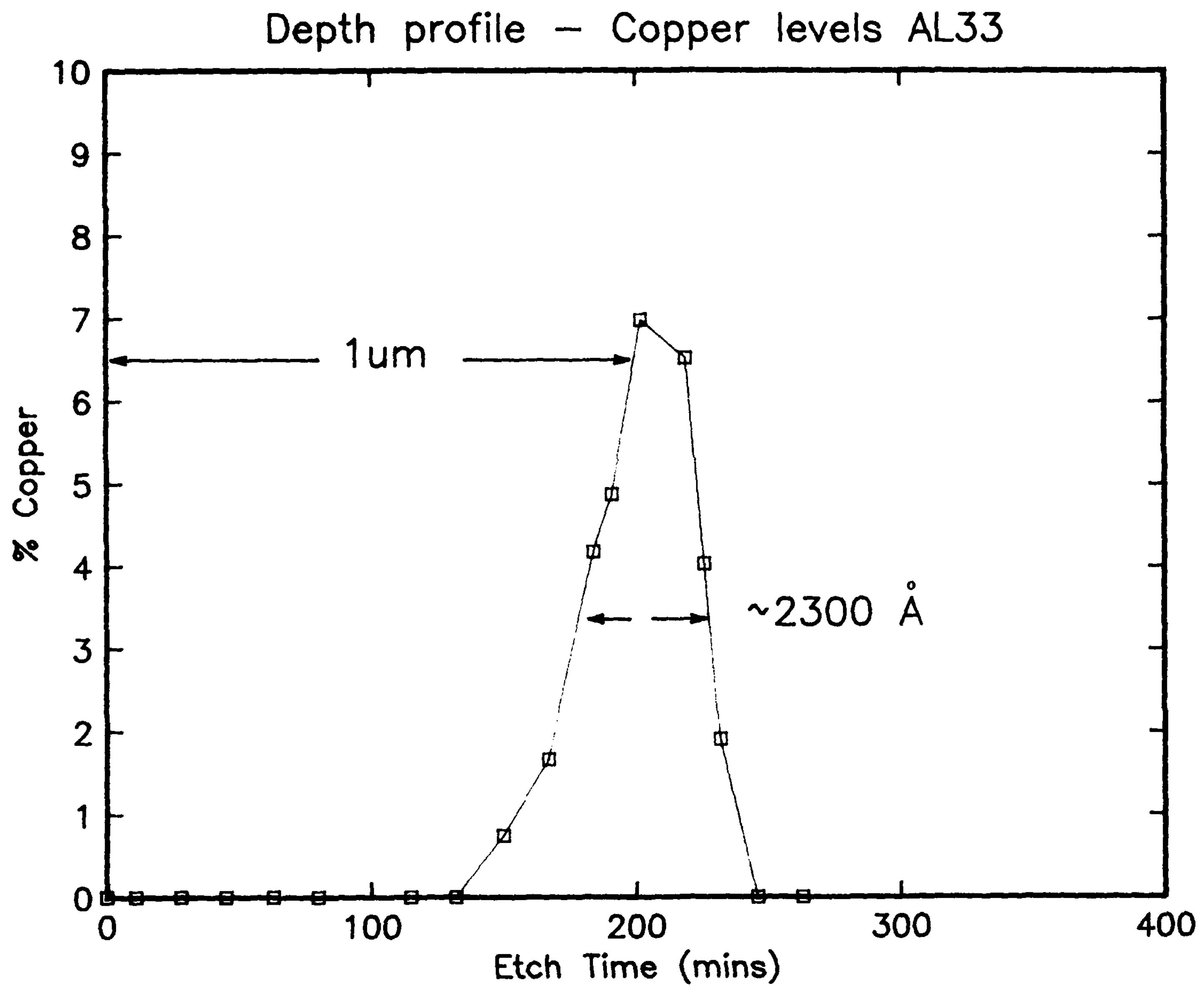


FIG.9

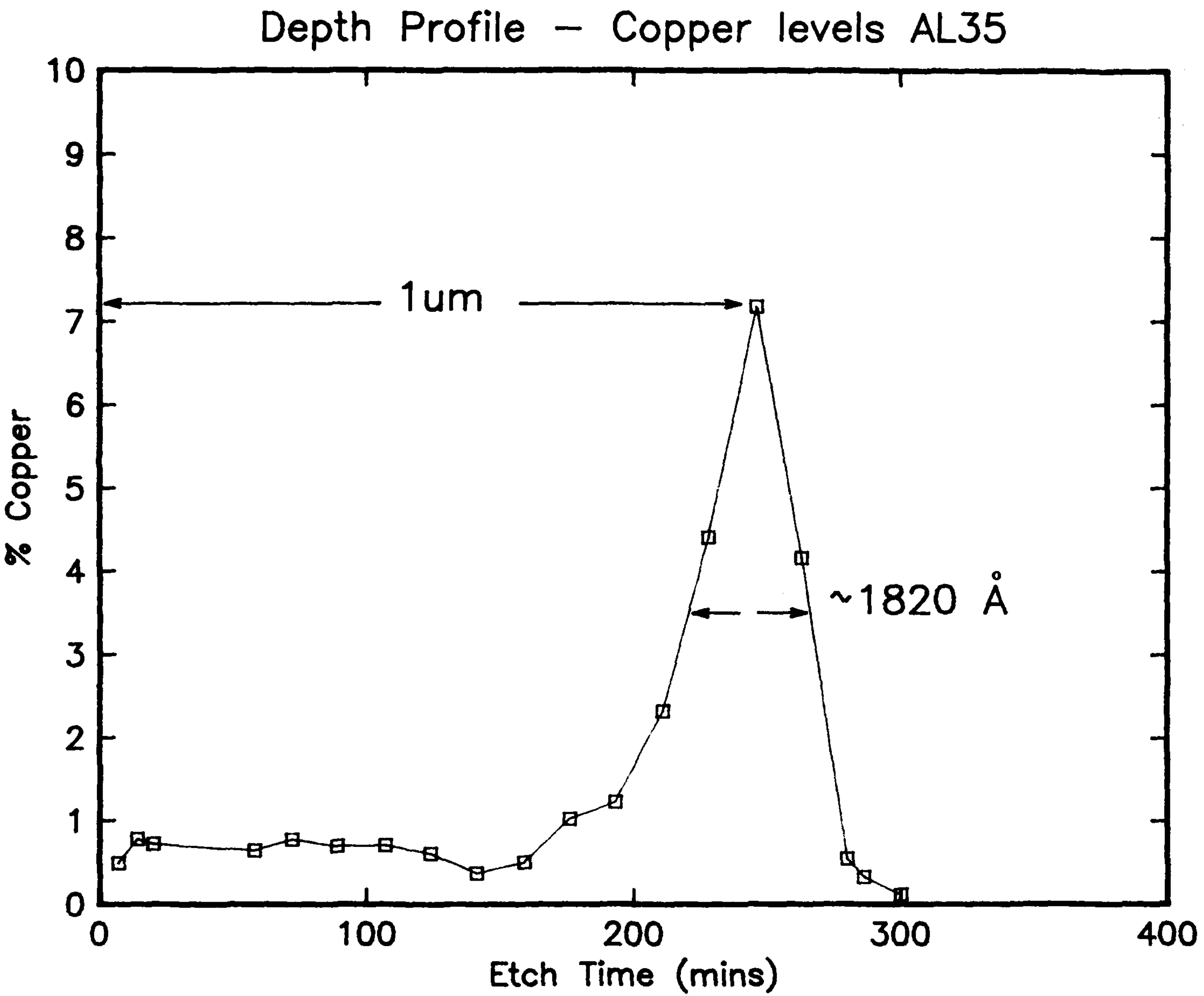


FIG.10

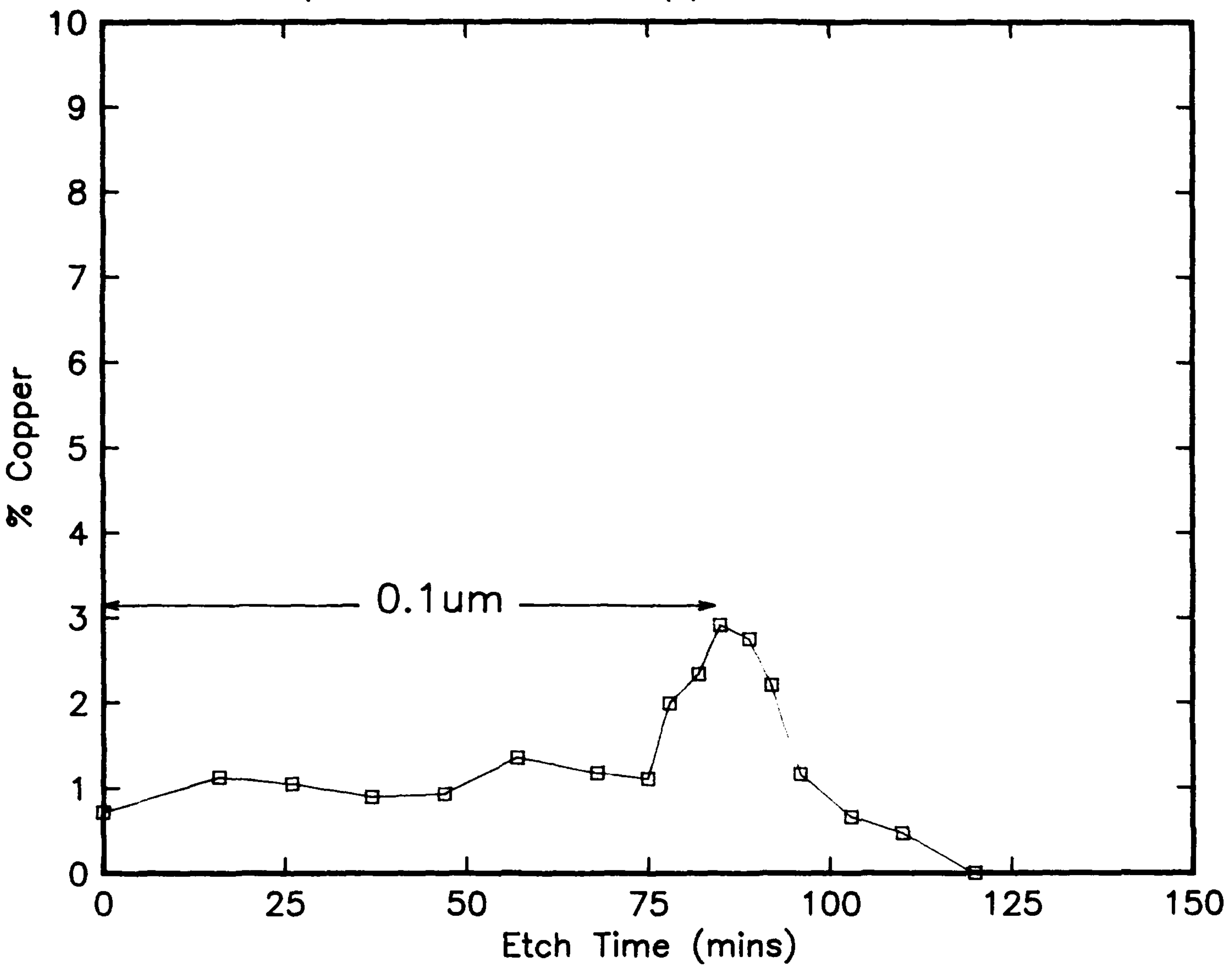


FIG.11

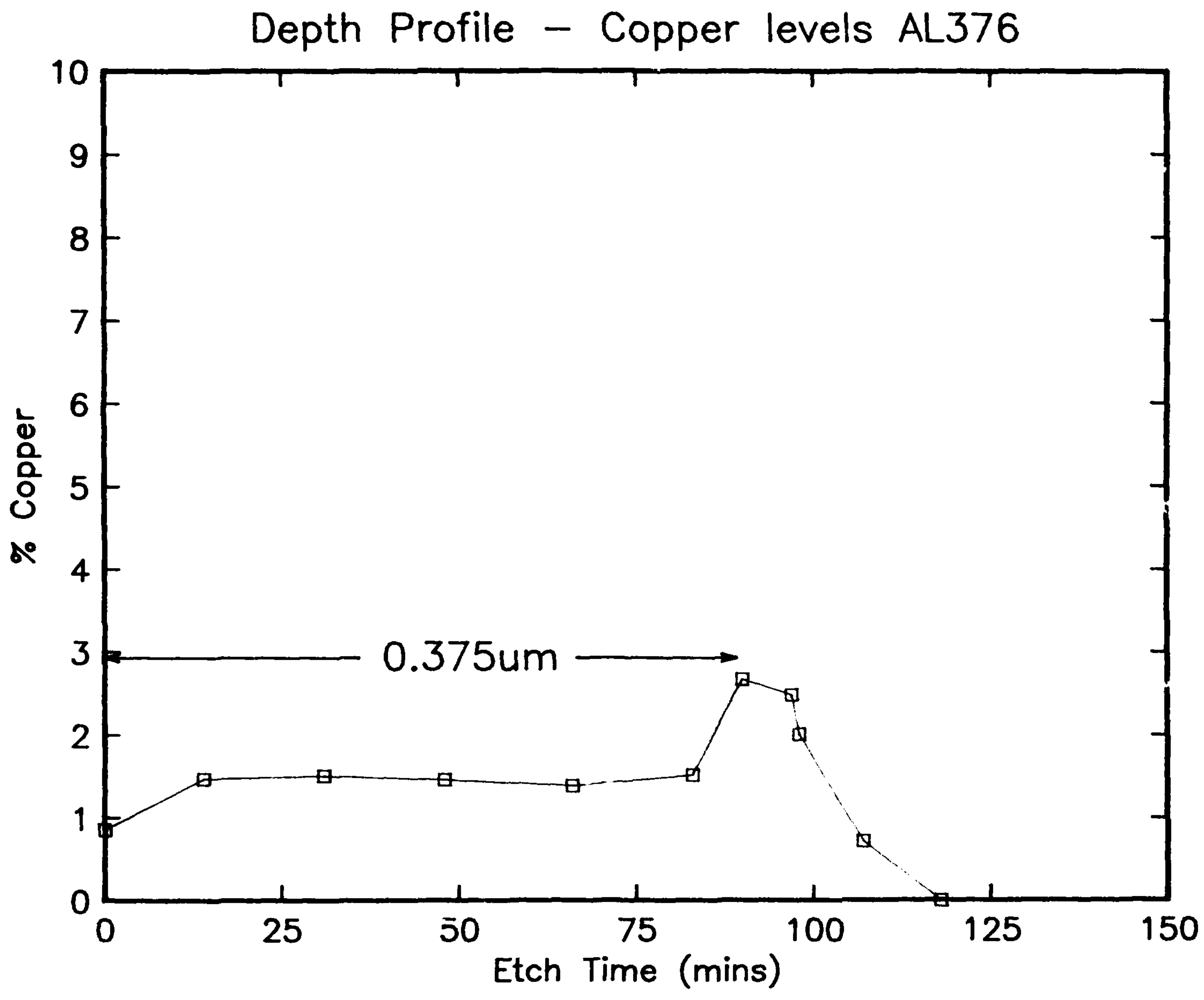


FIG.12

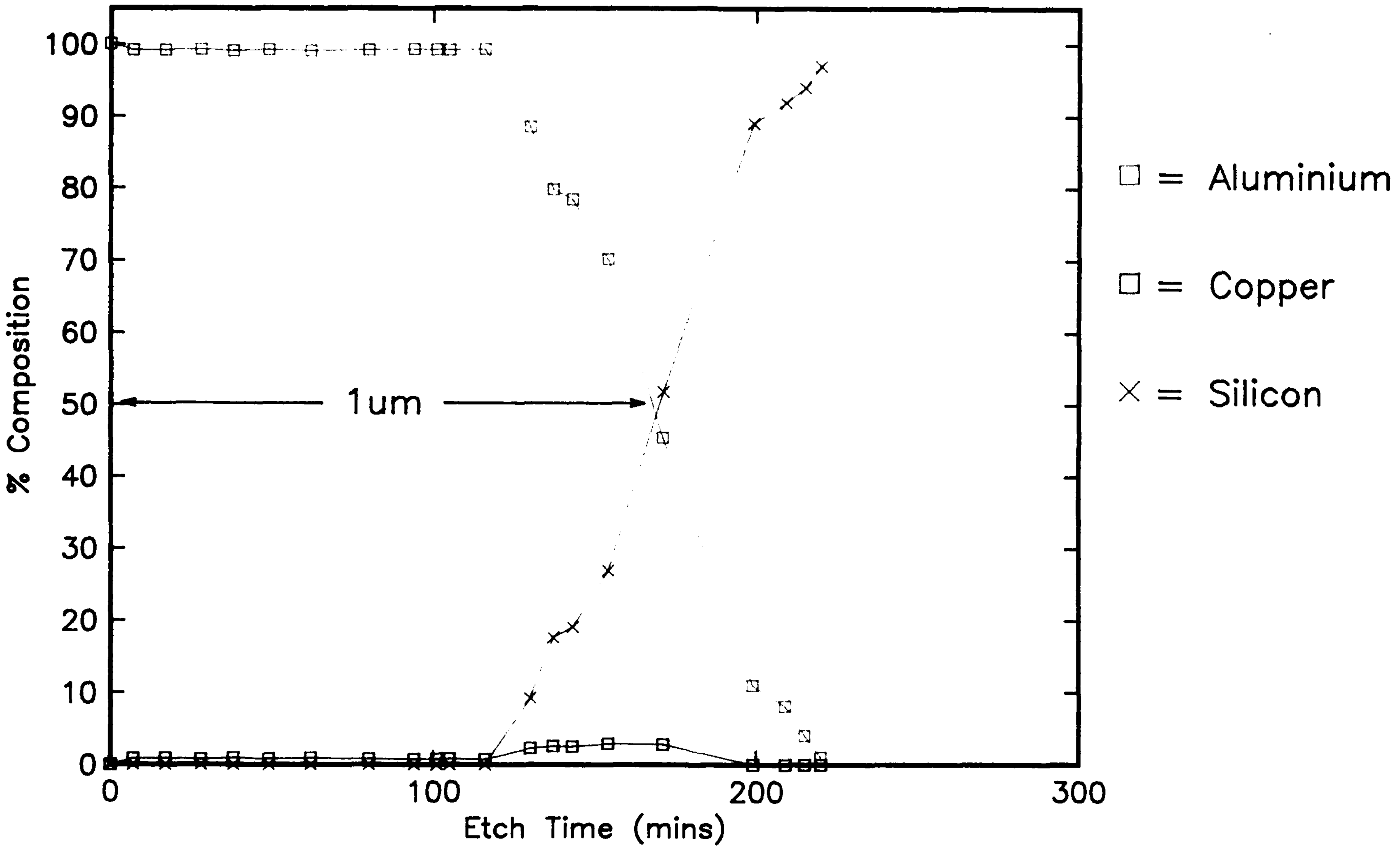


FIG.13

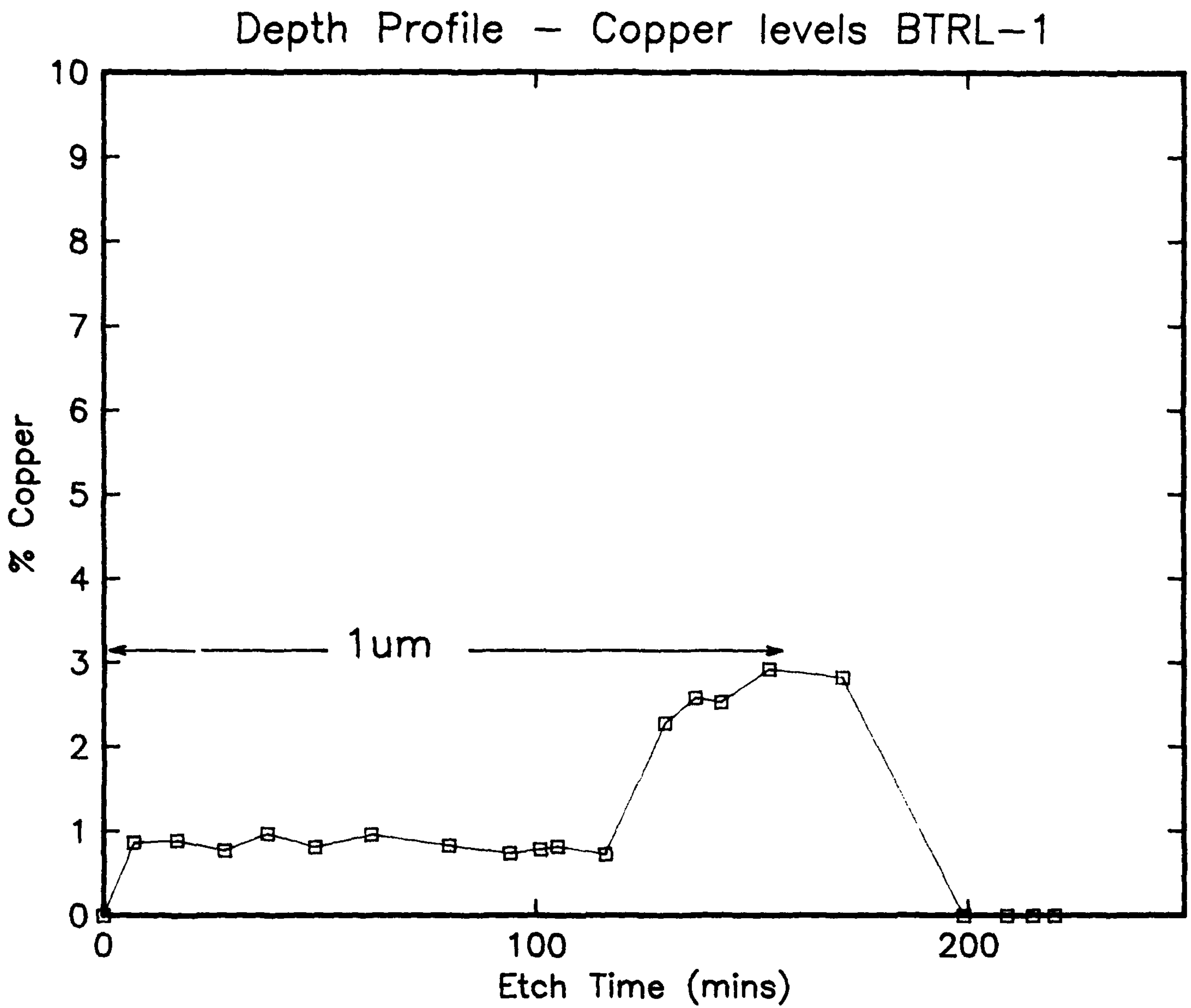


FIG.14

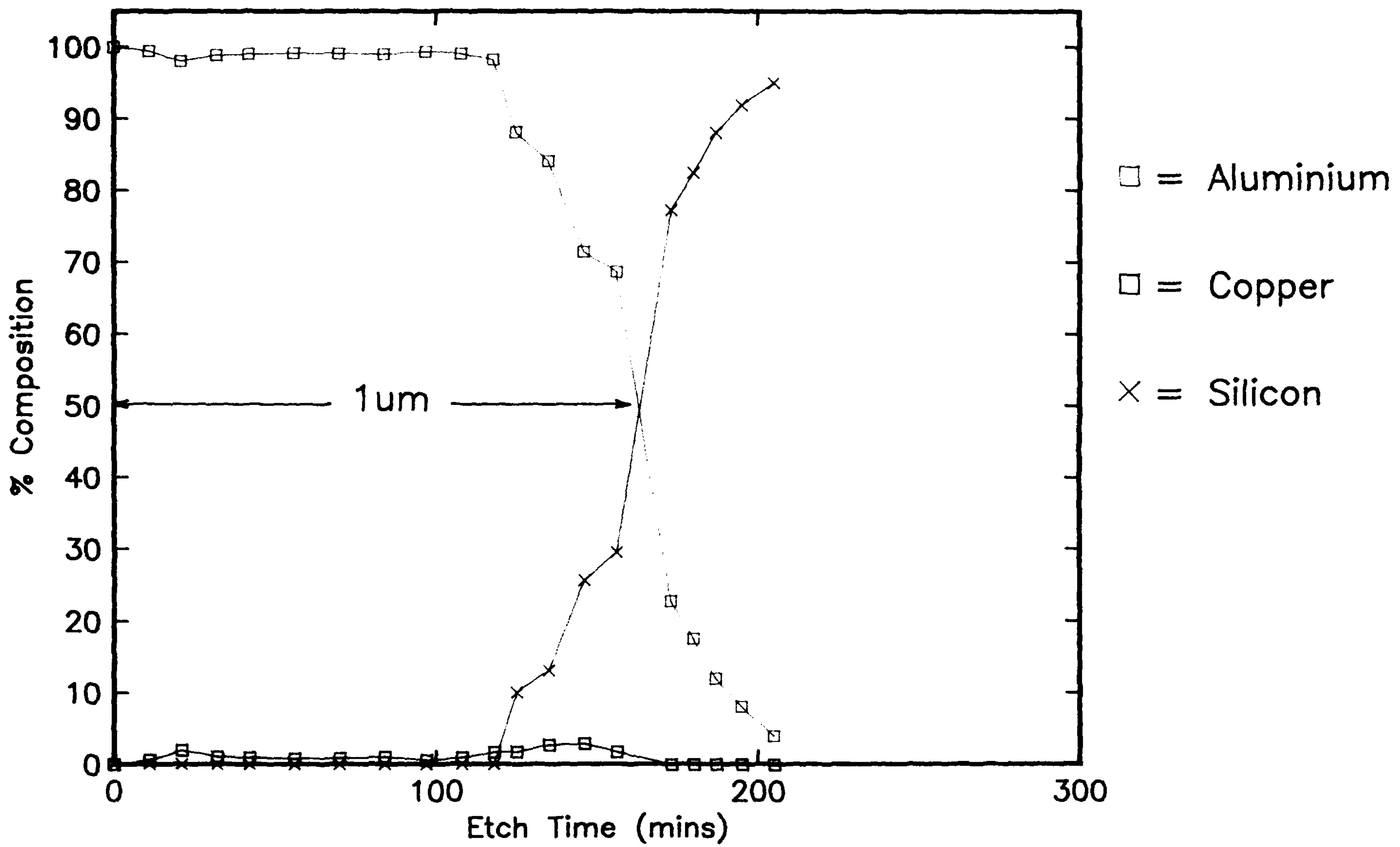


FIG.15

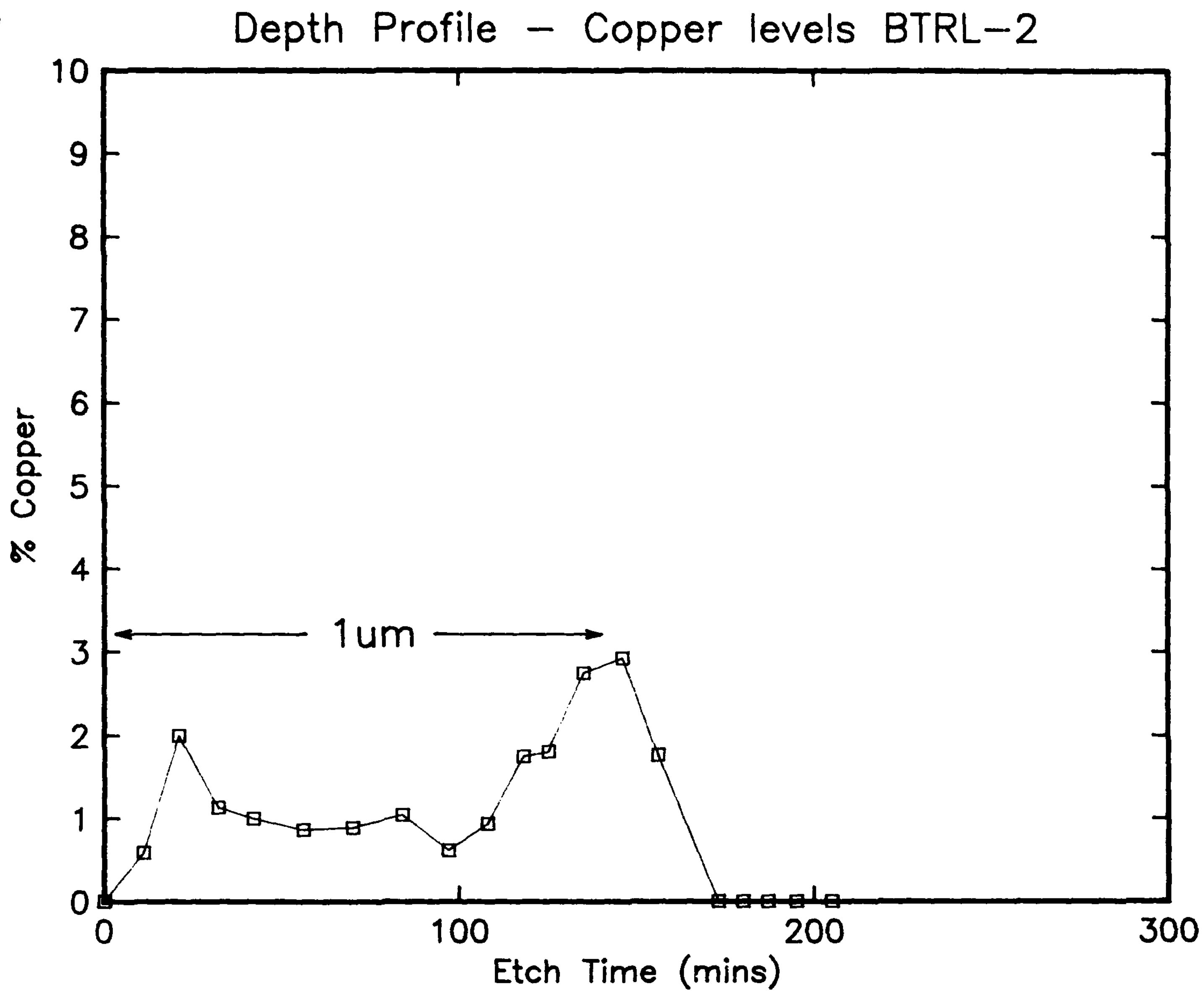


FIG.16

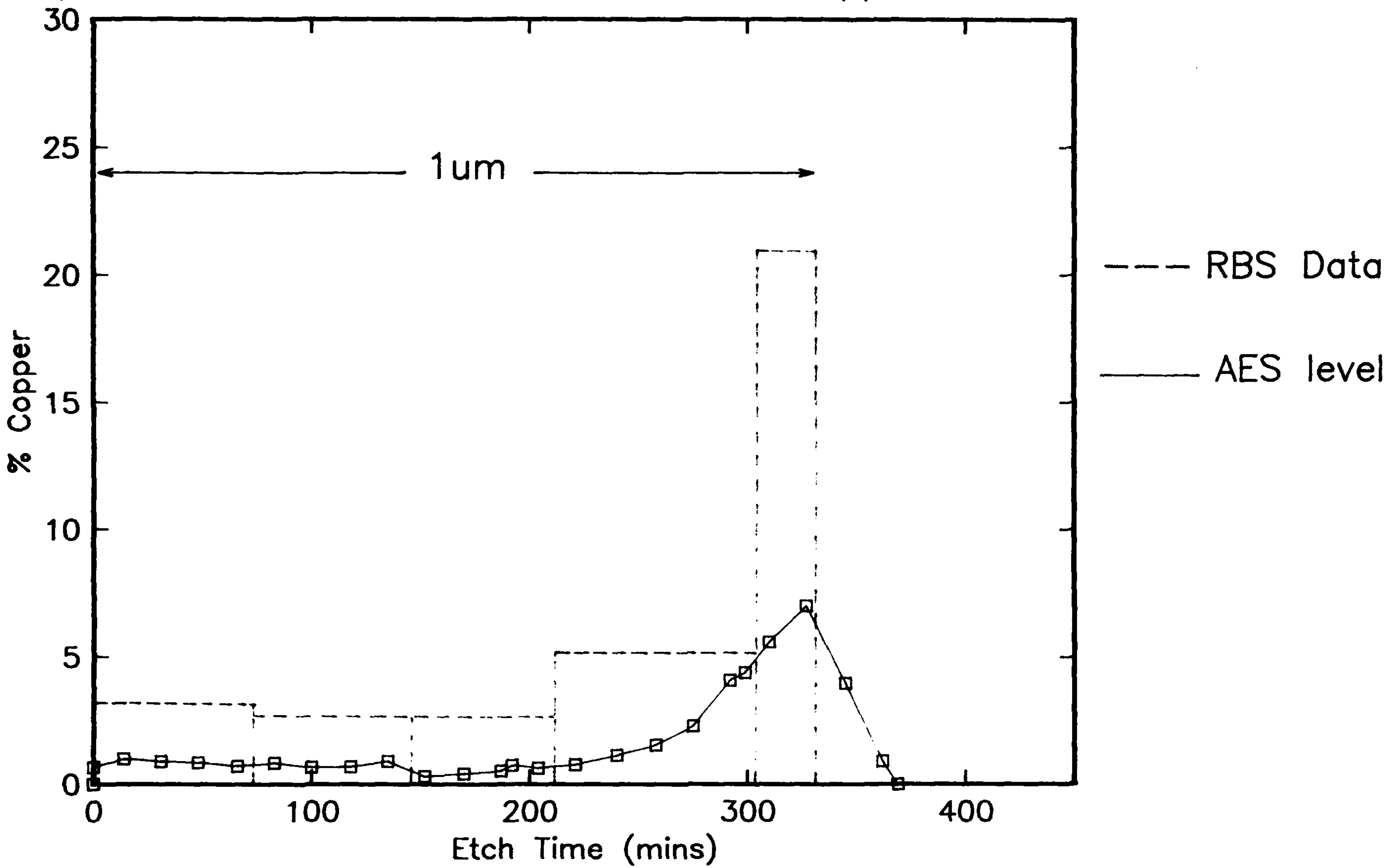
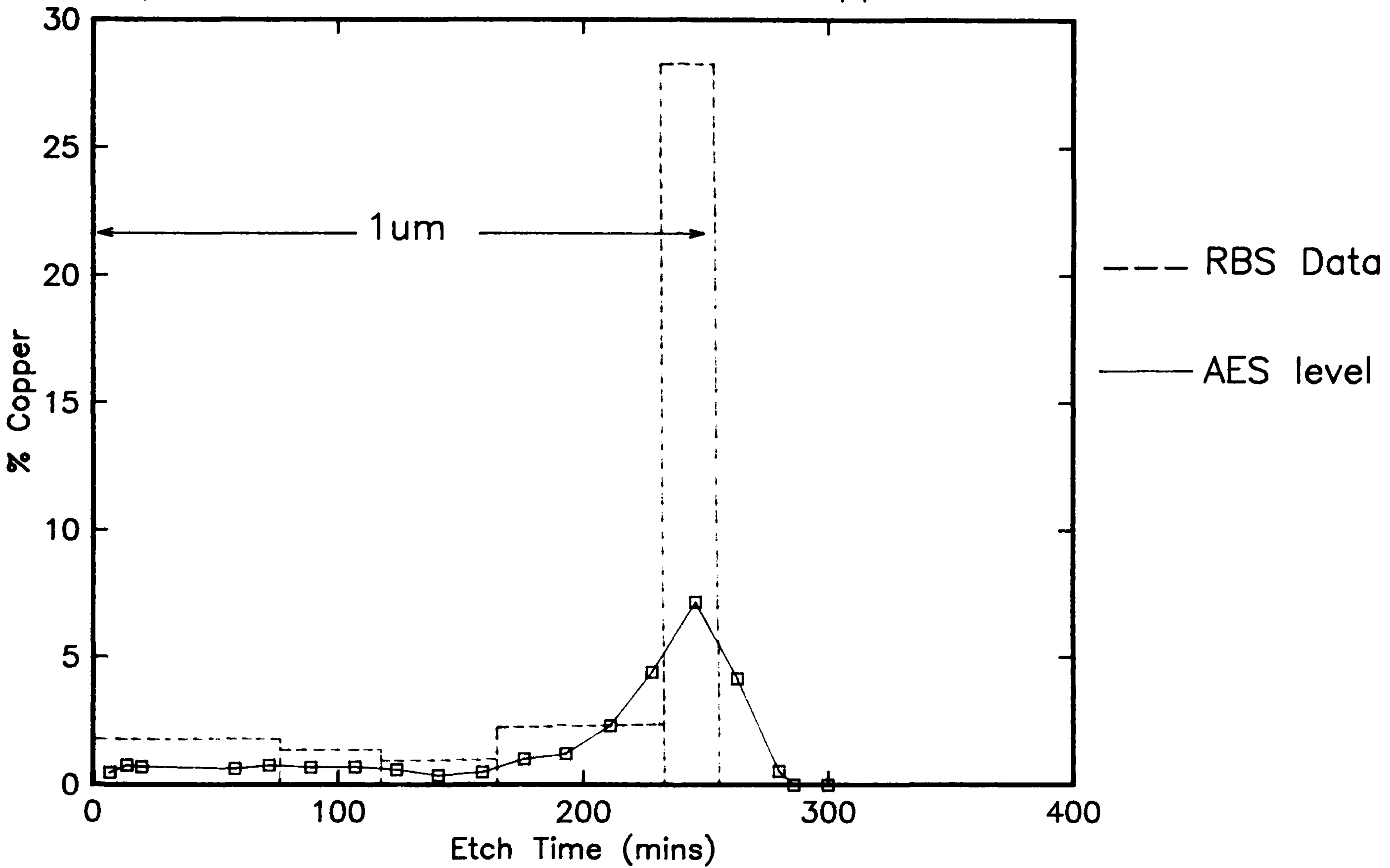


FIG.17



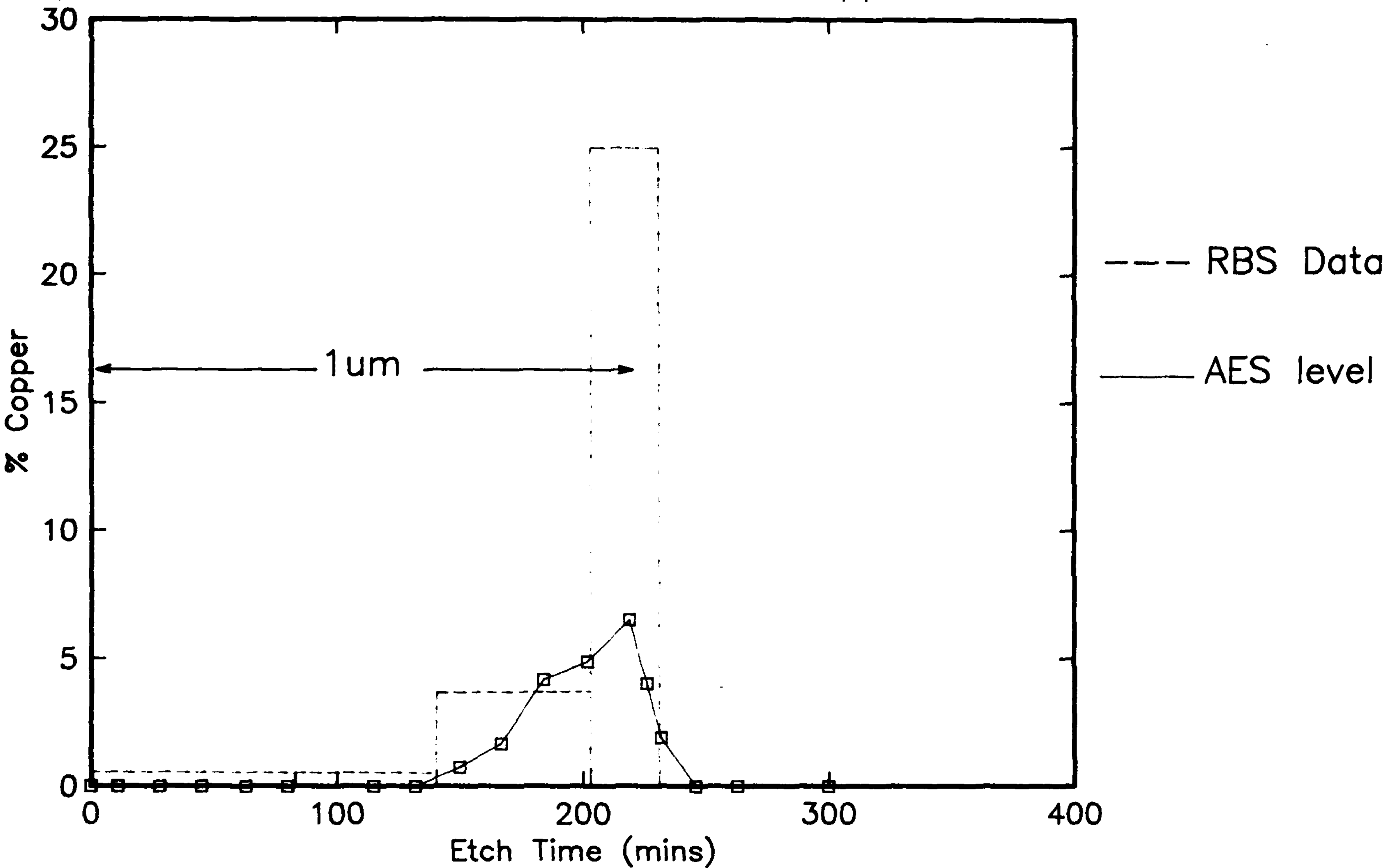


FIG.18
Depth Profile and RBS data overlaid – Copper levels AL33
% Copper
Etch Time (mins)
1um
RBS Data
AES level
0
5
10
15
20
25
30
100
200
300
400

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GREEN, M A; RODWAY, D C	30

Abstract

A study has been made, using Auger Electron Spectroscopy (AES), of copper copper segregation in Aluminium-Silicon-Copper films processed in the Silicon Processing and Evaluation Laboratory (SPEL). The AES technique and its interpretation are briefly discussed. A description of the Auger Spectrometer and experimental details are also provided.

The effects of variations in layer thickness and annealing temperatures on the interface between the Al-Si-Cu and the silicon substrate were studied. Results obtained from other samples from British Telecom research laboratories, and alternative analysis methods such as Rutherford Backscattering (RBS) are also discussed and conclusions drawn as to the nature of this segregation.

Abstract Classification (U,R,C or S)
U

Descriptors

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