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LA-UR-87-214

CONF-870725--

FEB 0 1987

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LA-UR--87-214

DE87 005099

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SUBMITTED TO ANALYSIS '87, The Microbeam Analysis Society (USA), to be held at Kailua-Kona, Hawaii, July 13 - 17, 1987.

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SURFACE ANALYSIS OF TITANIUM COATED SILICONE RUBBER BIOLOGICAL IMPLANTS

J. D. Farr and W. B. Hutchinson

A wide variety of materials are used today in the fabrication of biomedical implants. Various plastics, ceramics, metals, and composites are found in dozens of applications as biomaterials. The biological interactions between the implant surfaces and the proteins and cells of the body sometimes cause problems such as inflammation, thrombosis, and encapsulation. Coating the implants with a biocompatible material such as titanium[1] could alleviate these problems. In an effort to improve the biological compatibility of silicone rubber vascular grafts, thin layers of titanium were sputter deposited onto medical grade silicone rubber. The surfaces of two such samples were then characterized by Auger electron spectroscopy (AES), electron spectroscopy for chemical analysis (ESCA), electron probe microanalysis (EPM), and ion microprobe mass analysis (IMMA).

Specimens and Methods

The Ti coating on one implant was expected to be about 200 angstroms thick, and the other about 500 angstroms in thickness. The original purpose of the analysis was to determine the oxidation state of the Ti on the surface, and

to determine the thickness of the coatings. The implants were about the size and shape of medicine capsules. The instruments used in this study were a Physical Electronics (PHI) Model 550 ESCA/SAM, a CAMECA MBX, and an Applied Research Laboratories IMMA.

Analyses and Results

Preliminary examinations - 200 angstrom coating

The sample was first analyzed in the ESCA/Auger system. ESCA and Auger survey spectra obtained from the as-received surface showed mainly carbon, oxygen, and silicon on the surface, along with low concentrations of titanium. High resolution scans were taken over the C1s, O1s, Si2p, and Ti2p regions in order to estimate atomic concentrations and assign binding energies to the major elements. The results indicated titanium dioxide and oxidized silicon, probably as silicone rubber. The analysis area was about 3 mm in diameter and 20 angstroms deep along one side of the implant. Concentration estimates, based on sensitivity factors[2] for this region, in atomic percent were: carbon -- 42.5, oxygen --35.3, silicon --20.5, and titanium --1.5. The ESCA survey for this area can be seen in Fig. 1a. Other areas analyzed showed variations in surface titanium concentrations. The Auger survey spectra seen in Fig. 1b was obtained from an area high in titanium --perhaps 20 atomic %. It shows the distinctive Auger lineshape for titanium dioxide.[3] The

sample was lightly sputtered with 1kV Ar ions in order to remove surface contamination, and Auger and ESCA survey spectra were again obtained. The results indicated silicon rubber, so it was assumed that either the titanium coating had been lost, or it was being masked by some surface material similar to the substrate. The specimen was then removed from the system in order examine it with a light microscope. The implant still had a metallic appearance over most of its surface, but showed cracked and convoluted features at 200X.

Electron and ion microprobe examination.

The low level of titanium initiated examination with the electron microprobe because of its greater sensitivity for titanium. Since the range for electrons in titanium far exceeds the expected 200 angstroms (8000 angstroms at 7Kev) a control was prepared with 200 angstroms of titanium evaporated on quartz. Intensity ratios for silicon and titanium were recorded (while rastering over a 50 X 50 micron area) in three different locations along the tube wall, and some variation was observed. Similar surveys were run on the control. The results indicated the titanium film on the sample was of greater thickness than that of the control. Microscopic examination of the sample's surface indicated it was not suitable for any type of quantitative results.

The electron probe results prompted examination with the ion microprobe. Using a 28N+ beam at 14 Kev while rastering

over a 110 X 80 micron area, mass scans were collected. Hydrogen, carbon, sodium, aluminum, silicon, and titanium were detected. Silicon and titanium were the most abundant. Depth profiles for silicon and titanium were run in a few locations. Only one species could be monitored at a time, therefore the silicon and titanium profiles were actually taken in adjacent areas. The results of the depth profiles indicated a relatively thin surface layer containing significant amounts of silicon. As sputtering continued, this layer was depleted and the titanium reached a maximum. Profiles for titanium on the control indicated the titanium layer on the sample was probably less than 400 angstroms thick. Making some assumptions[4] about the sputter rate for silicon, the surface layer was probably less than 100 angstroms thick.

Further Examinations - 200 and 500 angstrom coatings

Auger survey spectra were obtained from the sample coated with 200 angstroms of titanium at increasing depths from the original sample surface by sequentially sputter etching and surveying the freshly exposed surfaces. The results shown in Fig. 2 indicated silicon, carbon, and oxygen in the first 100 angstroms or so at nearly the same levels seen in silicone rubber, along with low titanium concentrations. At a depth of about 150 angstroms, silicon levels dropped, and titanium levels increased, mostly in the form of titanium dioxide. Further sputtering revealed a

layer composed of carbon, titanium, silicon, and oxygen at about 300 angstroms. Finally, at about 400 angstroms, the silicone rubber substrate was exposed. It was not possible to be precise about the depths sputtered on the sample, since the sputter rate estimates were based on the control sample which had a different geometry and substrate. Also, the method of titanium deposition was different on the control.

The sample coated with 500 angstroms of titanium was compared to an uncoated silicone rubber specimen. ESCA and Auger surveys of the as-received surfaces of both of these samples showed only minor differences between the coated and uncoated specimens. An Auger depth profile obtained from the coated sample is shown in Fig. 3. Titanium and oxygen are again closely associated, as are carbon and silicon. The emerging picture of the coating on these samples is as follows: the outermost layer, less than 100 angstroms thick, composed of silicon, carbon, oxygen, and traces of titanium, along with silicone rubber and oils; next, a layer about 550 angstroms thick, composed of oxides of titanium and carbon; then a layer about 250 angstroms thick, composed of oxides of titanium, carbon, and silicon; and finally, the silicone rubber substrate.

The crater produced by the ion beam during sputter profiling was about 2 mm in diameter. An ESCA survey obtained from the crater area showed carbon, oxygen, silicon, and titanium. A scan over the Ti2p level, seen in Fig. 4, shows titanium in at least three different chemical states.

Following charge correction based on the C1s and Ar2p3/2 lines,[5] and curve fitting using PHI software, binding energies of 453.5 eV, 456.0 eV, and 458.5 eV were obtained for the major (Ti2p3/2) peaks. The peaks at 453.5 and 459.9 eV indicate titanium metal and possibly titanium monoxide. Titanium dioxide is responsible for the peaks at 458.5 and 464.4 eV, and the peaks seen at 456.0 and 462.5 eV could be assigned as a titanium-hydrocarbon complex. The sum of all six fitted curves is shown, as well as the original data.

Conclusions

There was an advantage in being able to use several techniques in analyzing these specimens. The electron and ion probe examinations provided a relatively fast, qualitative view of the nature of the samples prior to the more detailed analysis by Auger and photoelectron spectroscopy. The surface of these samples is complicated by the creeping of components of the silicone rubber substrate through the titanium coating. Some evidence of diffusion is present, as shown by the Auger depth profiles, but probably the major route is through defects in the titanium coating. The long chain dimethyl silicone polymers which make up silicone rubber could break up into various low molecular weight silicon compounds, creep up through pinholes in the titanium coating and cover the surface. This creeping and diffusion causes the titanium-containing overlayer to be nearly twice as thick as that expected for the coating.

Titanium primarily exists in the tetravalent state throughout the coating. Compatibility studies are now in progress to determine the effects of these coatings in vitro.

The authors are in the Chemical and Laser Sciences Division of Los Alamos National Laboratory, Los Alamos, NM 87545. They gratefully acknowledge the assistance of Dave Duchane and Debbie Wrobleski in providing the specimens analyzed. This work is supported by the U. S. Department of Energy under contract W-7405-ENG-36.

FIG. 1.--(a) ESCA survey of as-received surface of 200 angstroms Ti sputter deposited on silicone rubber. (b) Auger electron survey spectrum from same sample over area high in Ti.

FIG. 2.--Auger surveys taken at increasing depths from surface of specimen coated with 200 angstroms of Ti: (a) top 100 angstroms, (b) at about 150 angstroms, (c) at about 300 angstroms, (d) at about 400 angstroms.

FIG. 3.--Auger electron depth profile of specimen coated with 500 angstroms Ti. Sputter rate was approximately 60 angstroms per minute.

FIG. 4.--High resolution spectrum from sputter crater showing three different chemical states of Ti.

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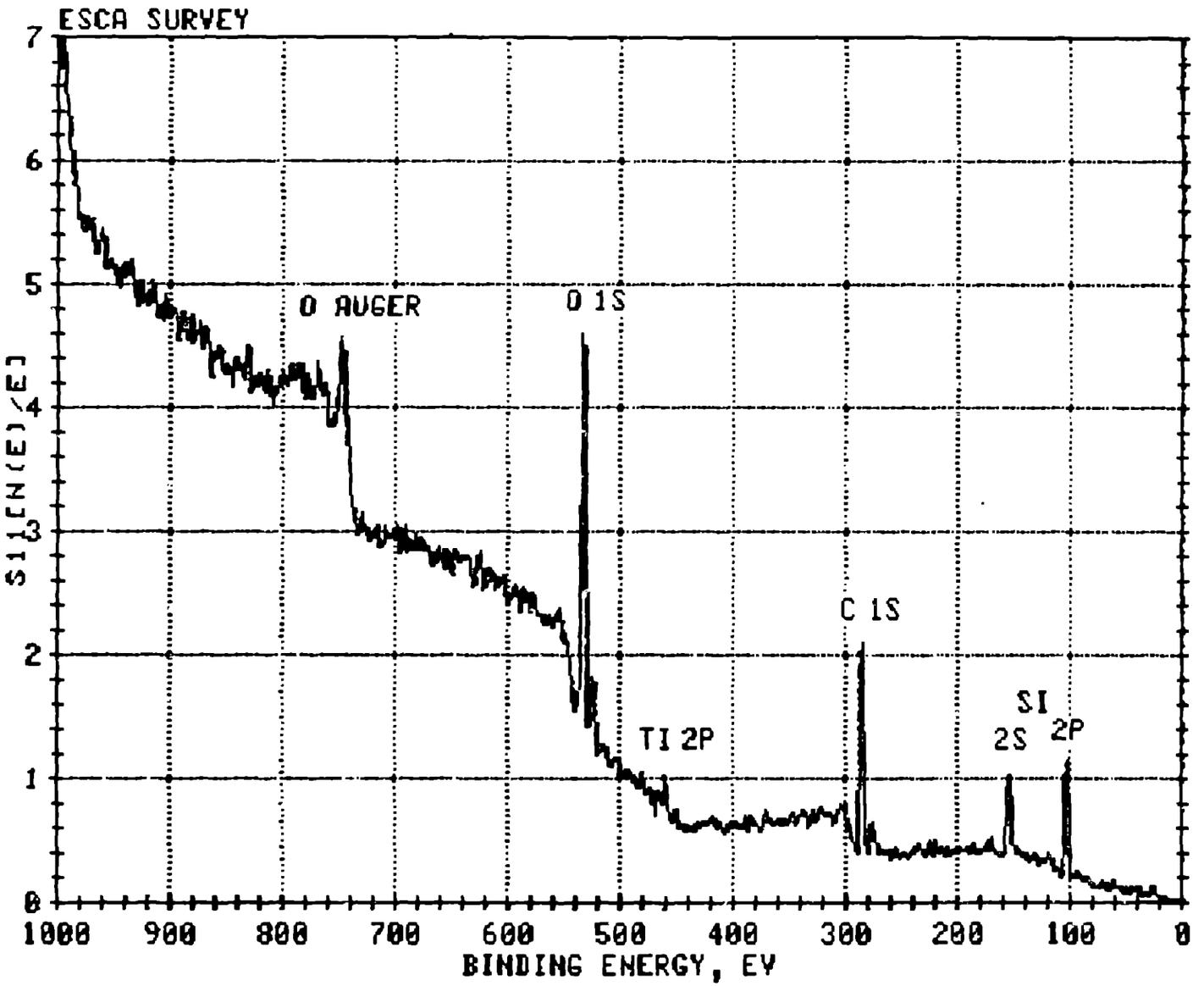
3. J. S. Solomon and W. L. Baun, Surface Science 51:228 1975.

4. G. K. Wehrer, "The Aspects of Sputtering in Surface Analysis Methods," in A. W. Czanderna, Ed., Methods of Surface Analysis, Amsterdam, The Netherlands: Elsevier Scientific Publishing Co., 1975.

5. D. M. Hercules, ESCA and Auger Spectroscopy, Washington, D. C.: American Chemical Society, 1979.


ESCA SURVEY
O AUGER
O 1S
C 1S
TI 2P
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BINDING ENERGY, EV
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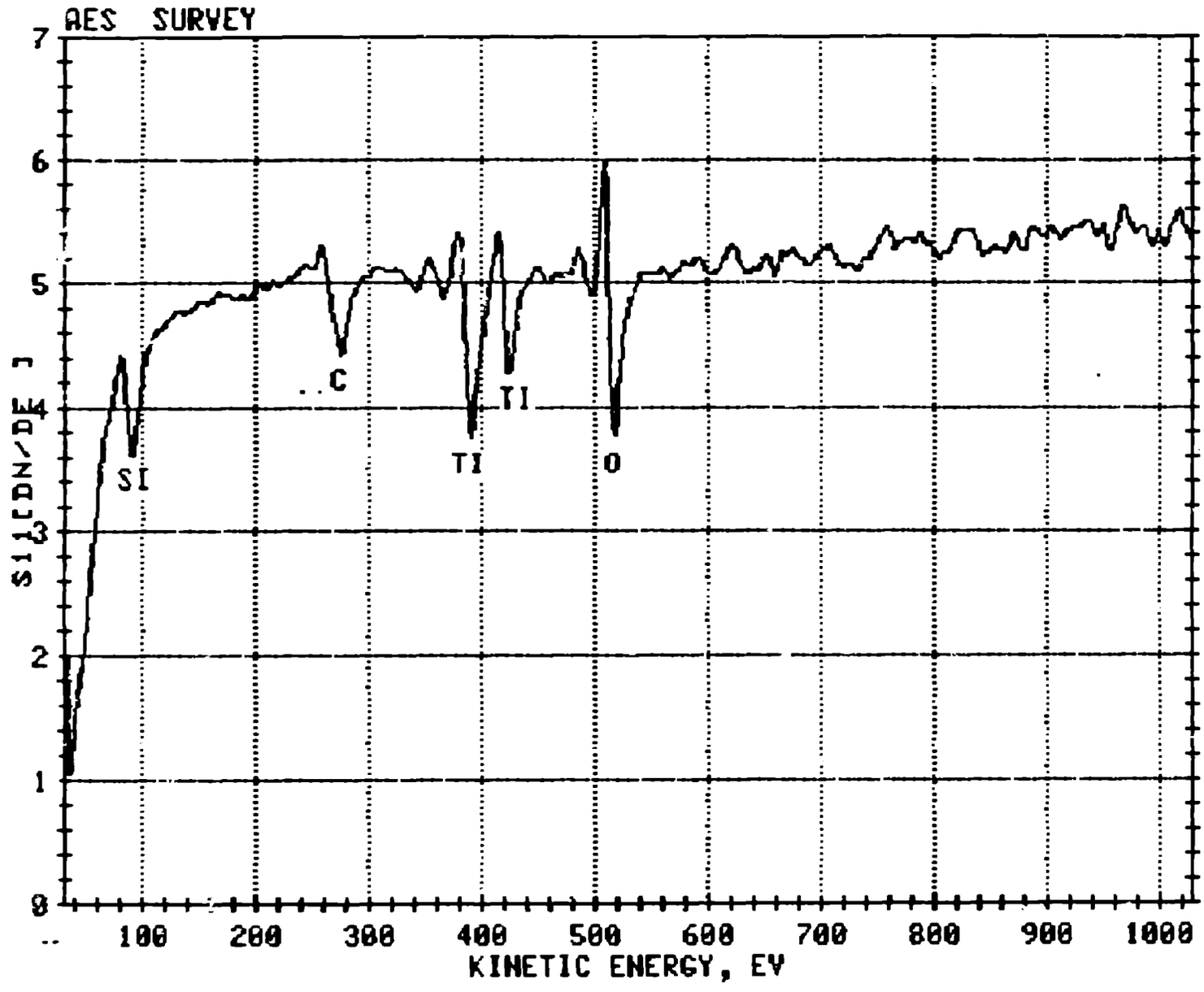
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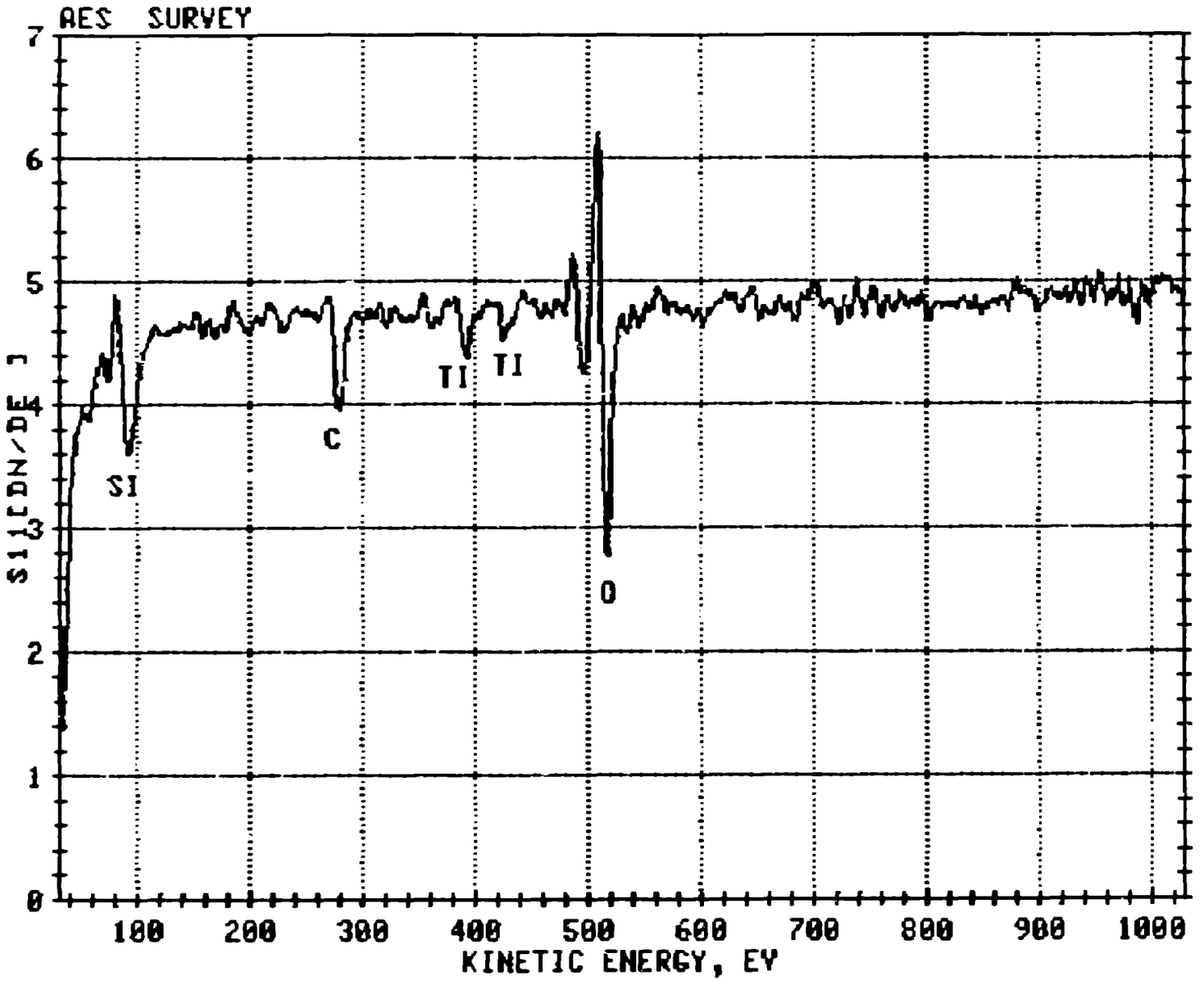
Fig. 2(a)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KINETIC ENERGY, EV

FIG. 2-b

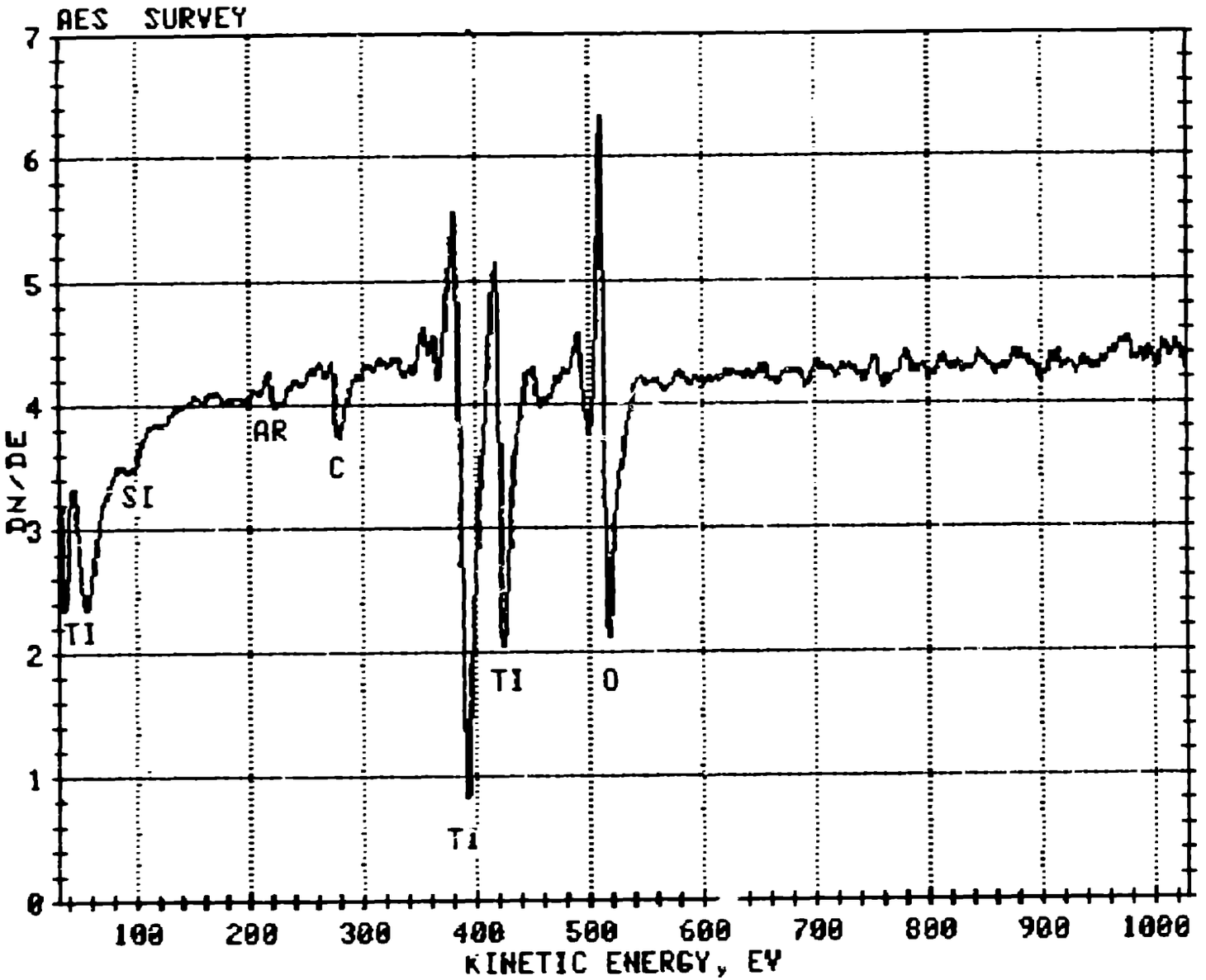
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FIG. 2c

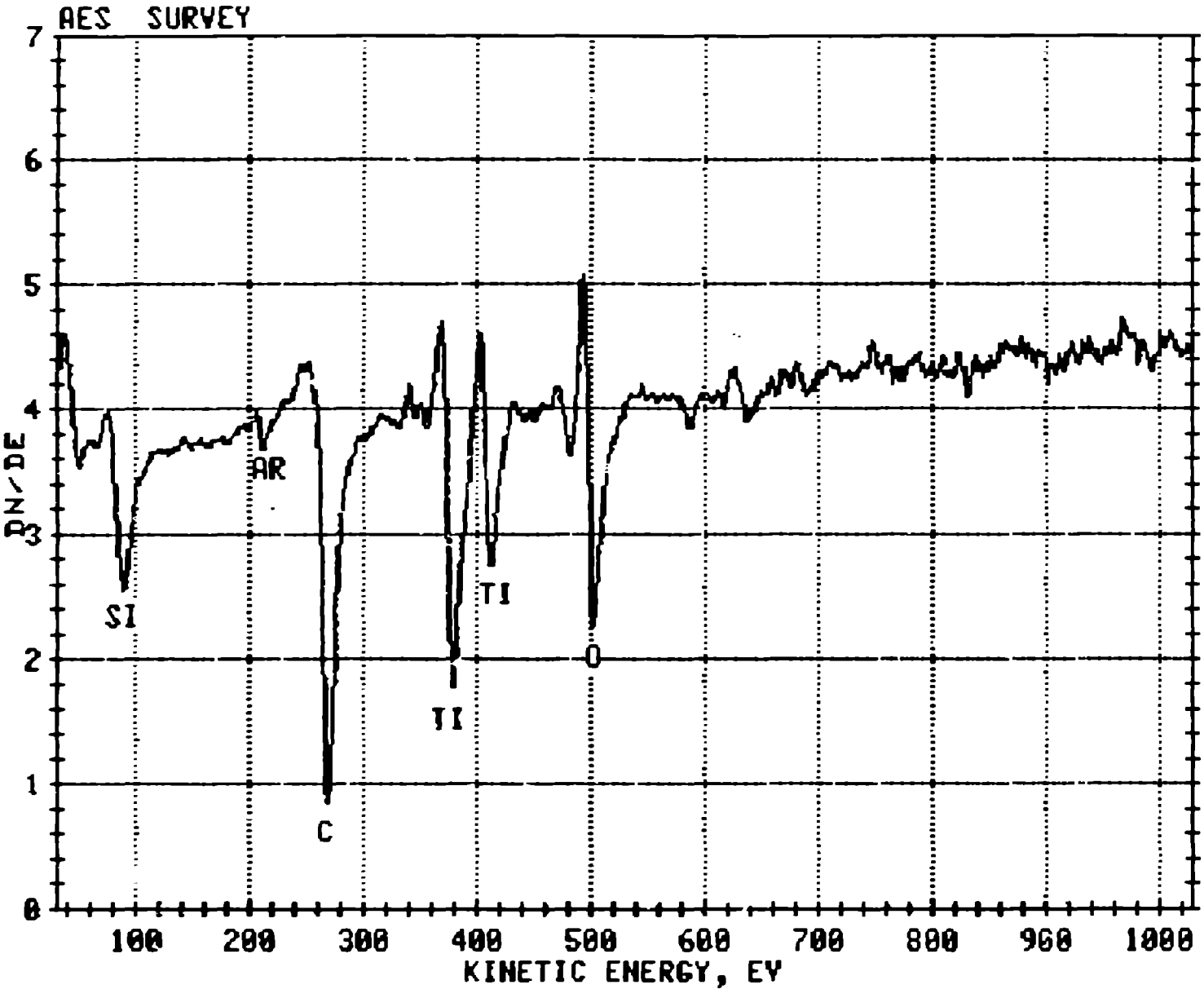
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FIG. 4

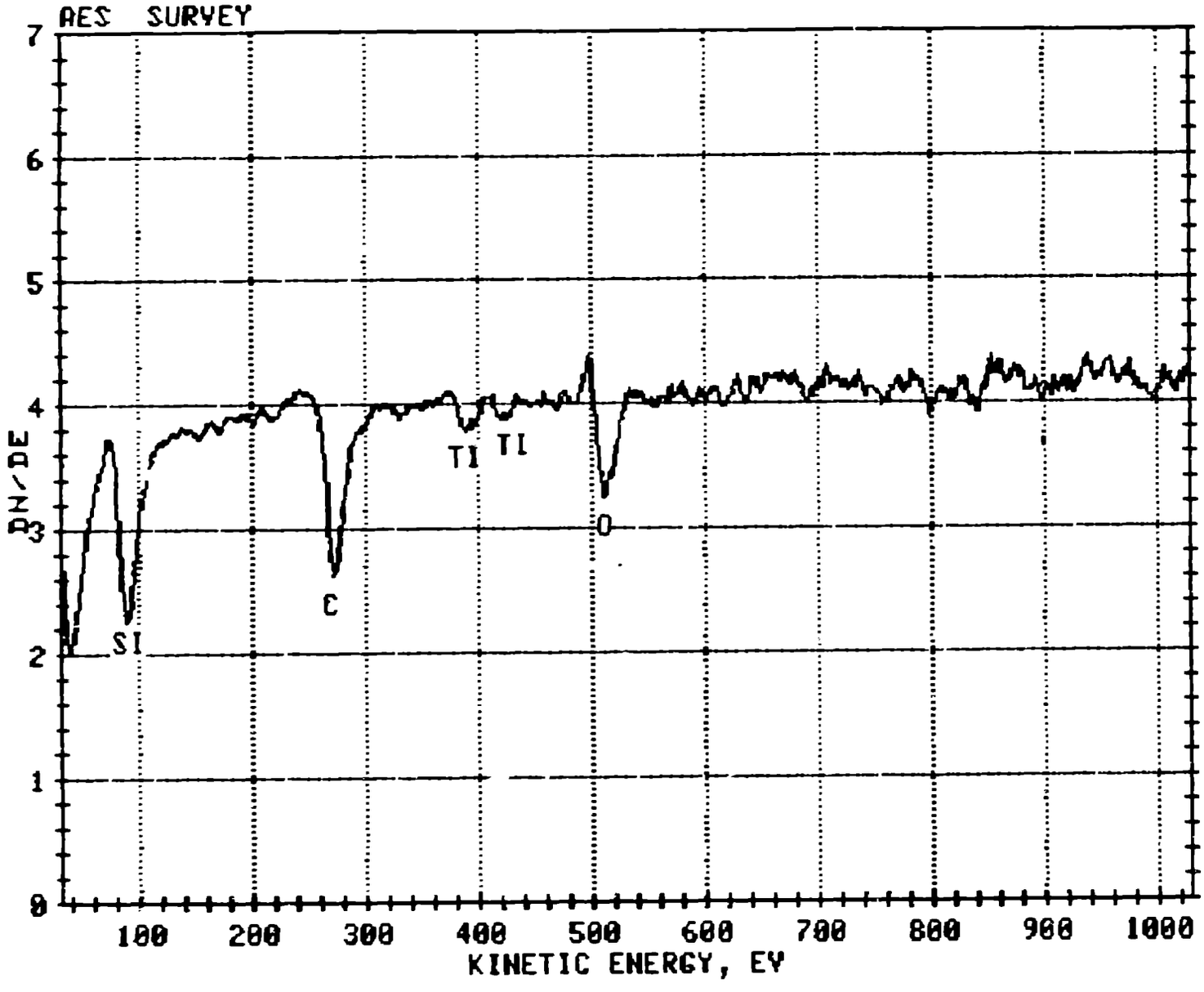
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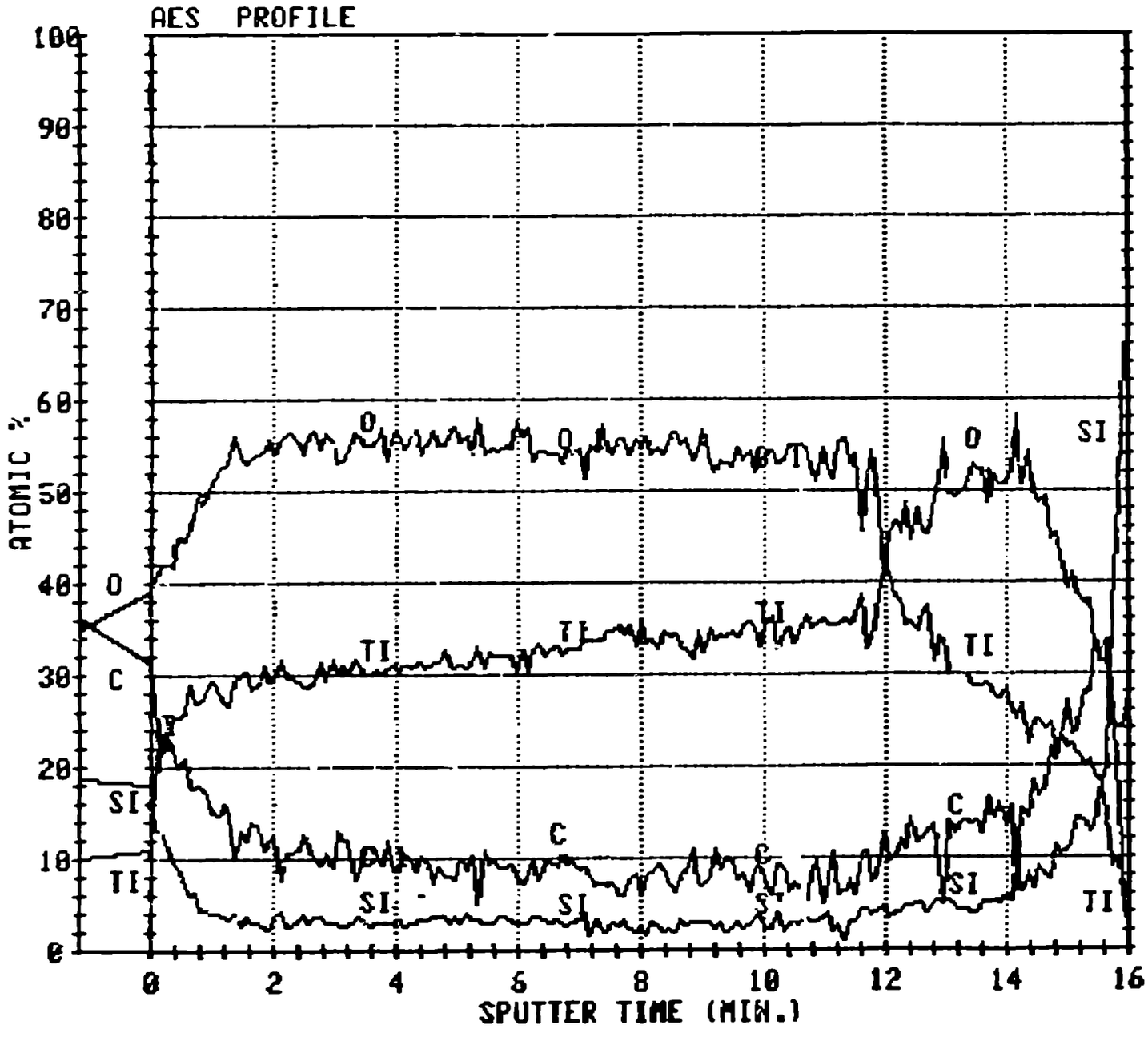
FIG. 3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SPUTTER TIME (MIN.)
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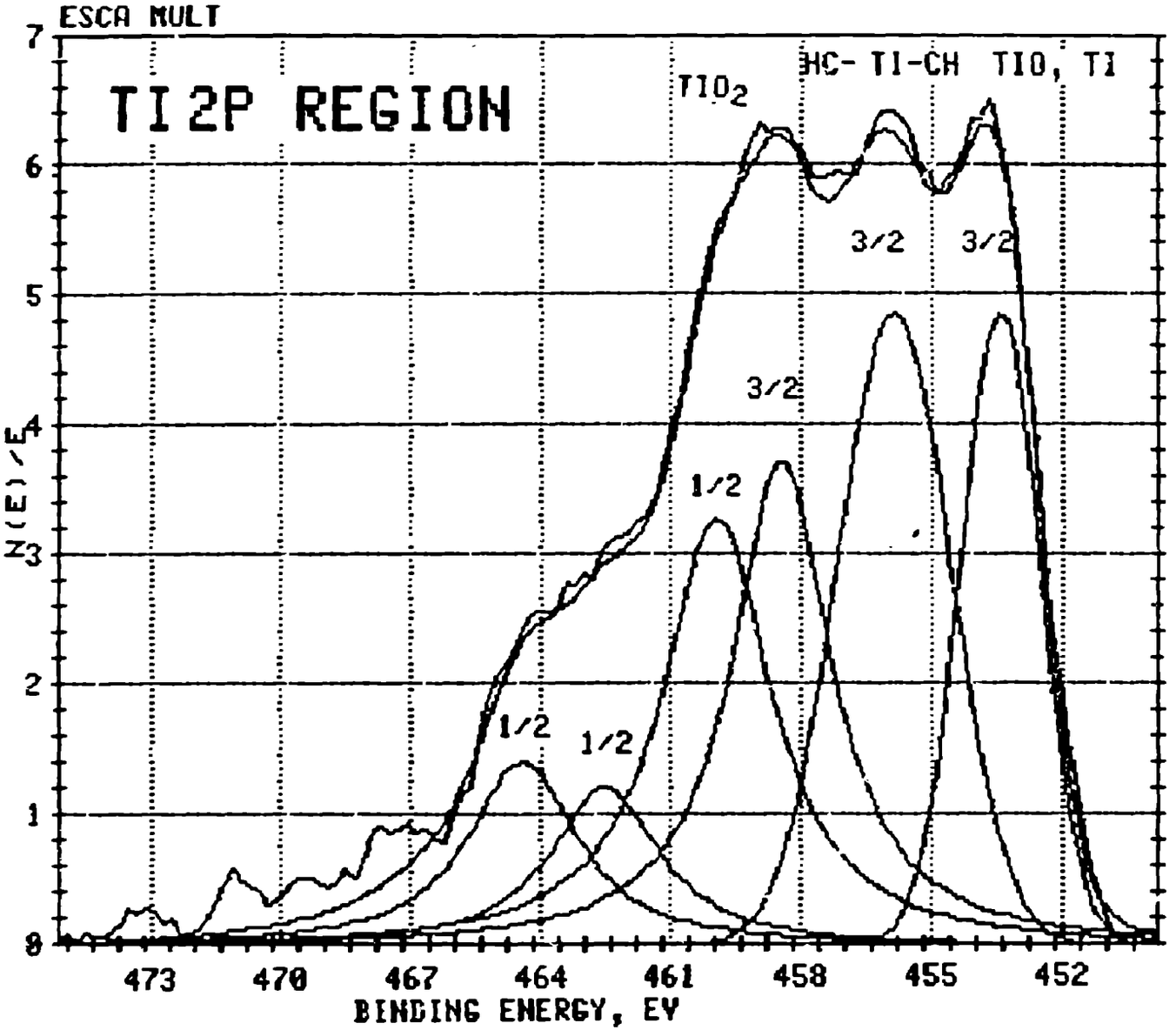
FIG. 4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458
455
452
BINDING ENERGY, EV