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Conf-911003--7

LBL-31000

AUG 19 1991

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To be presented at the The Metallurgical Society Conference,
Cincinnati, OH, October 20–24, 1991, and to be
published in the Proceedings

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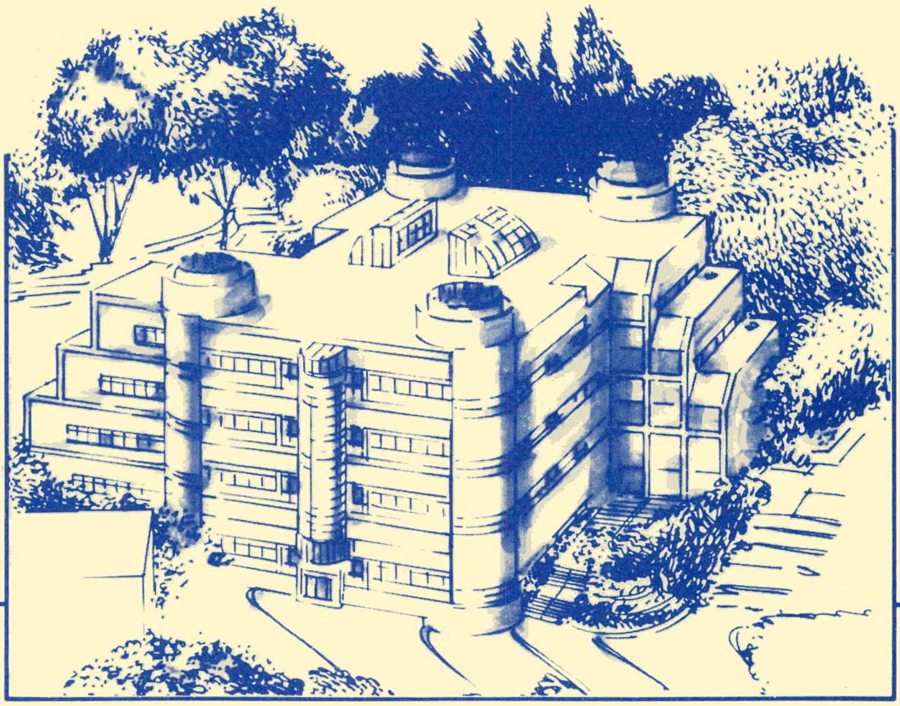

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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Preliminary Observation Of Carbon In Pre-Tinned Specimens

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July 1991

This work was funded by the Harry Diamond Laboratories of the U.S. Army under MIPR No.R91-056 , through the U. S. Department of Energy under Contract No. DE-AC03-76F00098

PRELIMINARY OBSERVATION OF CARBON IN PRE-TINNED SPECIMENS

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Abstract

Flux is generally applied on a metal surface before soldering to help clean the surface. The decomposed flux may evolve to the surface as dross or may remain in the molten solder. The motivation for this work is the observation of high concentrations of carbon in the surface of pre-tinned Cu-clad printed circuit boards, while other contaminants disappear after an initial sputtering. Four different surface conditions are analyzed using Auger electron spectroscopy. The results confirm that the presence of carbon in pre-tinned specimens is due to the use of flux. The effect of carbon on solderability is not yet known.

Introduction

Soldering is commonly used to join components in electronic packaging. A solder joint is made by bringing molten solder (usually Pb-Sn) into contact with a metal surface (usually copper or nickel) with which the solder forms a bond. However, oxidation is a continuing problem for many applications; a clean metal surface that is exposed to air spontaneously oxidizes to lower the effective solid-vapor tension (σ_{SV}), and is often poorly wet by solder after oxidation. Hence, it is common in the manufacture of electrical components to "pre-tin" metal surfaces that are to be soldered by coating them with a thin, protective layer of Pb-Sn solder. The pre-tinned layer protects the metal substrate from oxidation and contamination, and is, at least in theory, easily dissolved or wet by molten solder during the reflow process.

In both the pre-tinning and the reflow process, a flux must be applied before soldering that helps clean the surface of either the copper or the pre-tinned layer and adsorbs at the liquid-vapor interface, lowering σ_{LV} and raising σ_{SL}. A common flux used in the industry is mildly activated rosin-type, Type RMA, which is a complex form of hydrocarbon. As the flux cleans the surface, the decomposed flux may evolve to the surface as dross or may remain in the molten solder. As the impurities in the molten solder increase, solderability is known to decrease.[1]

Surface analysis of as-received pre-tinned Cu-clad printed circuit boards using Auger electron survey indicates high concentrations of carbon, while other contaminants such as oxygen and chlorine disappear after an initial sputter. Figure 1 shows Auger spectra of pre-tinned board before and after sputtering for 2 minutes. This paper attempts to identify the source of carbon and its effect on solderability.

Experimental Procedure

Sets of pre-tinned specimens were made with and without using flux to identify the source of the carbon. However, the general sample preparation was the same: oxygen-free, high-conductivity (OFHC) Cu coupons, 25.4 mm square by 0.84 mm thick, were used for the substrate. The Cu surfaces were mechanically polished using a 600 grit silicon carbide paper and chemically etched with nitric acid diluted 50% with water. The specimens were rinsed in water followed by ethyl alcohol. Then, a set of specimens was kept in RMA flux for 10-20 minutes prior to immersion in solder, while the specimens without flux were quickly immersed in Pb-rich (95Pb-5Sn) molten solder bath. The coupons were kept in molten solder for 5 seconds followed by air cooling. The 95Pb-5Sn solder bath was 360°C. The thickness of the pre-tinned layer was approximately 10 μm on all samples.

The surface analysis of fresh 95Pb-5Sn solder, Cu-clad board, and pre-tinned specimens was performed using Auger electron spectroscopy (AES).

Results and Discussions

All the specimens showed surface contaminants, but after an initial sputter, the only contaminant present was carbon. To determine the source of carbon, fresh 95Pb-5Sn solder and Cu-clad board were analyzed, as shown in Figure 2. The surface of solder was argon sputtered for 2 minutes and left in the chamber for 15 minutes prior to analysis to determine whether there was any carbon build-up from the chamber. The carbon peak at 272 eV was not observed (Fig. 2a). Similarly, the board after a minute sputtering showed mainly the Cu peaks (Fig. 2b). Figure 3 shows Auger spectra of pre-tinned specimens made with and without flux. The overall survey of the surfaces is similar except for the carbon peak. For the pre-tinned specimens made with flux the secondary Pb peaks at 249 and 267 eV have almost disappeared and only the carbon peak is apparent. The small carbon peak seen in the spectrum of pre-tinned specimen made without flux is from the re-used solder. These Auger spectrum confirm that the carbon is from the residual flux and not from the board or the solder. However, they do not indicate the carbon bonding state on the solder, although the shape of the carbon peak resembles graphite more than that of carbide. There is no known copper, tin, or lead carbide formation and the solubility of carbon in tin and lead is almost negligible.

Kumar and Moscaritolo[2] also detected high concentrations of carbon in discrete locations at the Cu-intermetallic interface by Auger analysis. While the precise effect of carbon contamination on wetting is not yet known, Chang[3] has shown that a carbon layer (700Å) is extremely effective as a diffusion barrier for Cu, in comparison to gold or nickel, because of the low chemical affinity between Cu and carbon. No out-diffusion of Cu through carbon was seen in his work, even after heat treatments as long as 72 h at 700°C. The carbon/Cu interface also showed adequate bonding.

Conclusion

The results of this preliminary work confirm the presence of carbon in pre-tinned specimens due to the use of flux. The effect of carbon on solderability is not yet known.

Acknowledgment

This work was funded by the Harry Diamond Laboratories of the U.S. Army under MIPR No. R91-056, through the U. S. Department of Energy under Contract No. DE-AC03-76F00098

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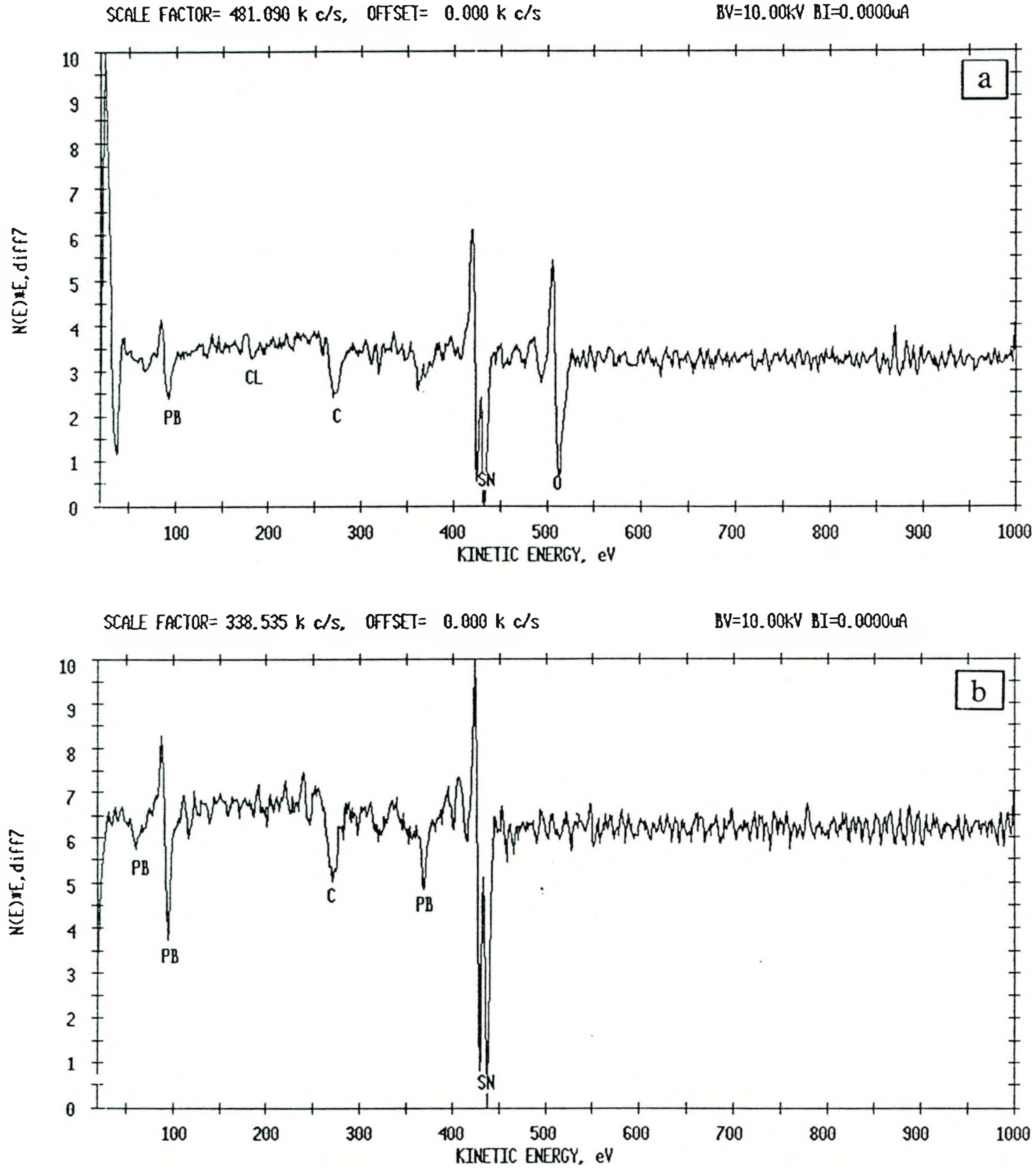

Figure 1: Auger spectra of pre-tinned Cu-clad printed circuit board: (a) as-recieved; (b) after two minute sputtering.

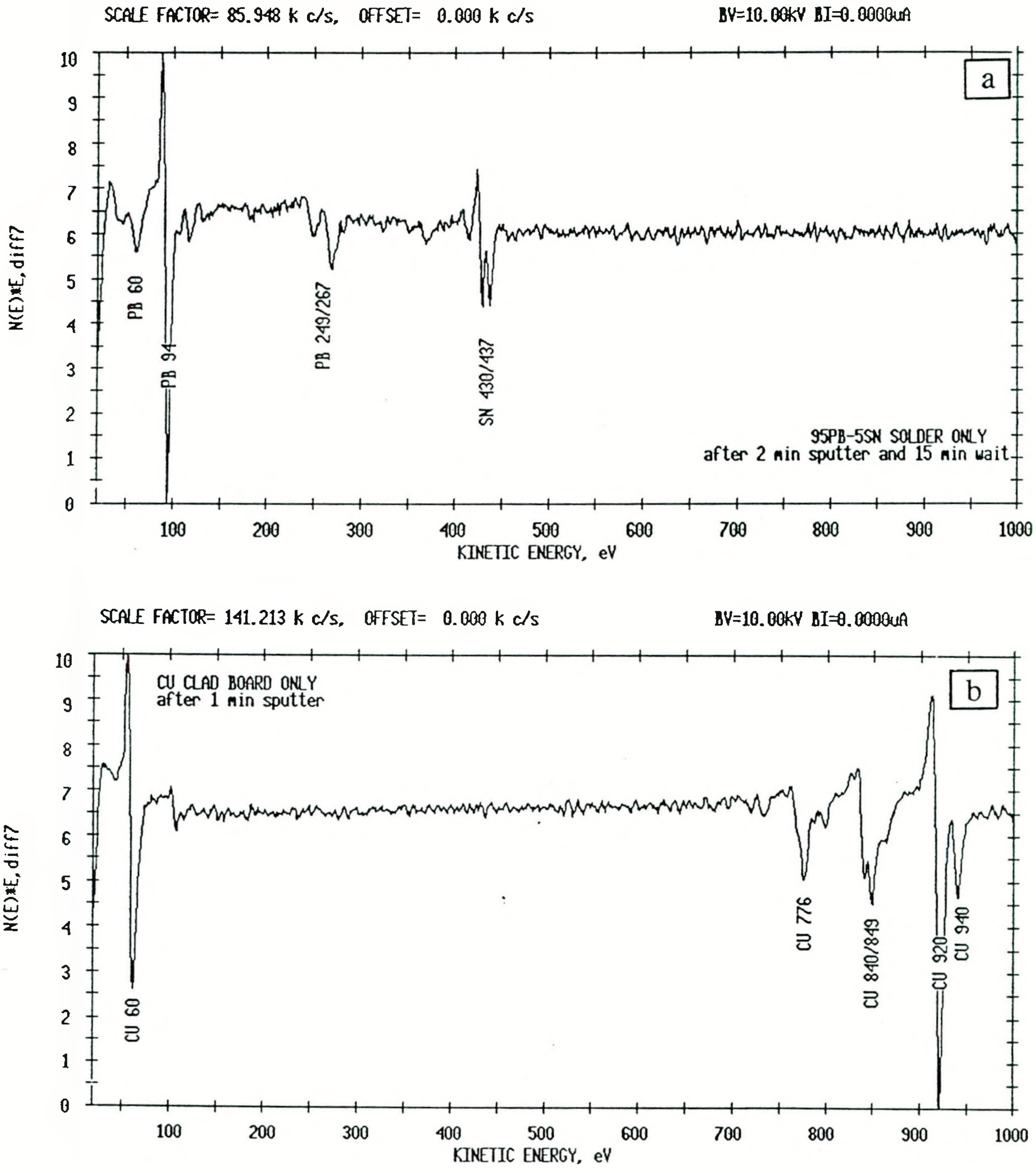

Figure 2: Auger strectra of (a) fresh 95Pb-5Sn solder, after two minute sputtering and 15 minutes in the chamber; (b) Cu-clad board, after a minute sputtering.

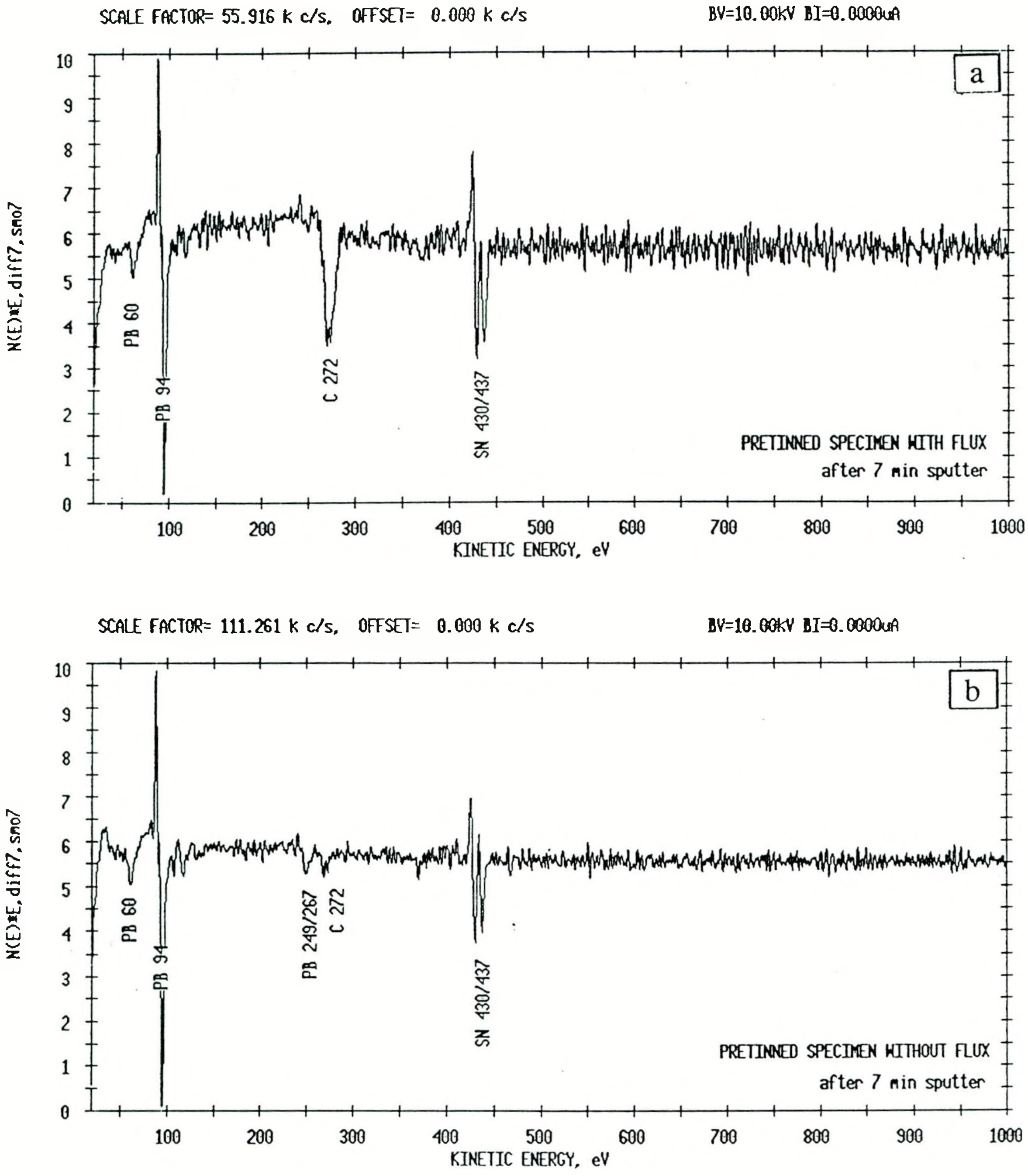

Figure 3: Auger strectra of pre-tinned Cu specimens made (a) with; (b) without RMA flux, after seven minute sputtering.

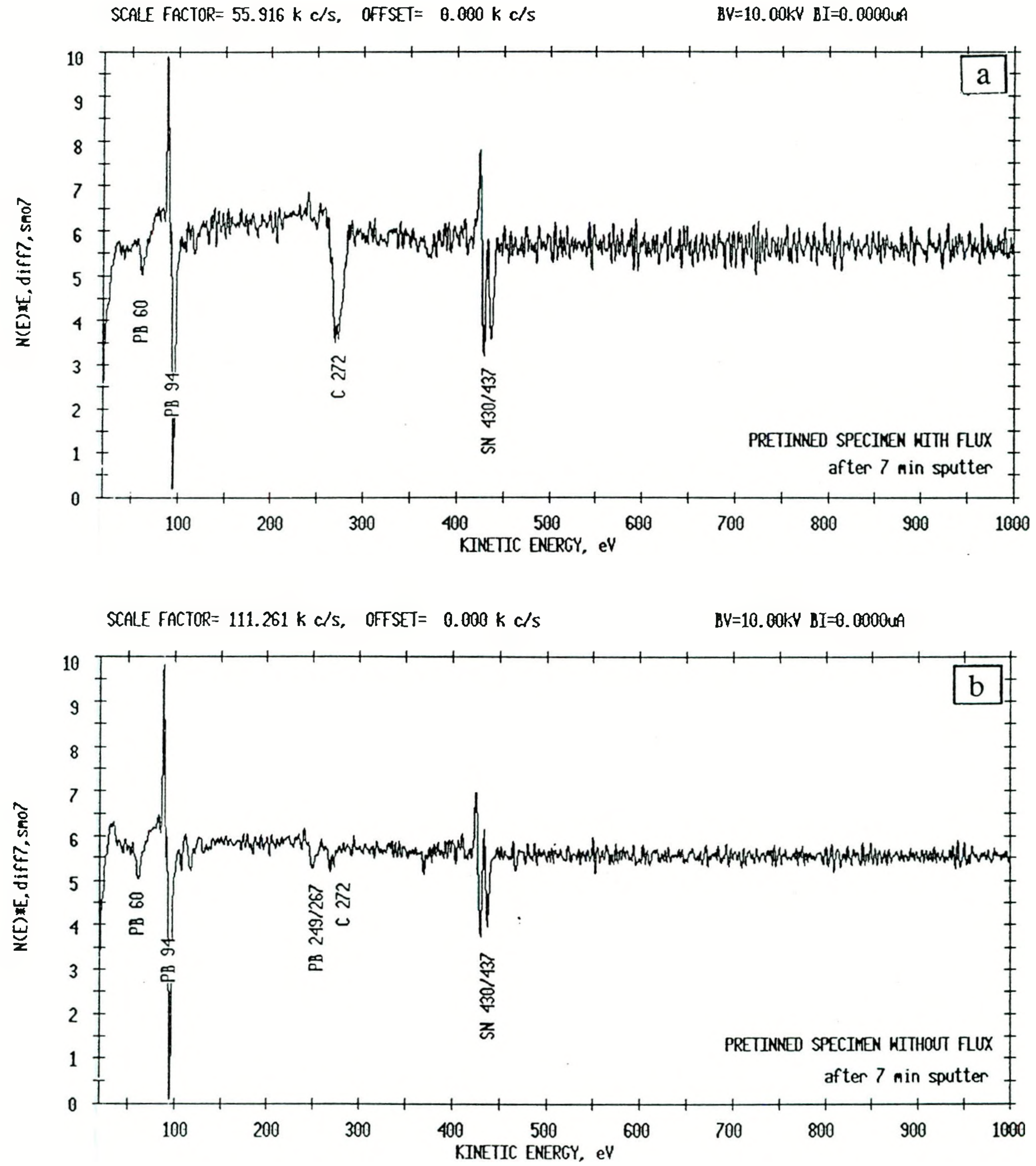

Figure 3: Auger strectra of pre-tinned Cu specimens made (a) with; (b) without RMA flux, after seven minute sputtering.

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