

LETTERS TO THE EDITORS

X-Ray Photoelectron Spectroscopy Investigation of Direct Process Contact Masses

INTRODUCTION

The modern silicone industry is based on the production of methylchlorosilanes using the direct process. The direct process, the reaction of elemental silicon with methylchloride, is catalyzed by the presence of copper (1). Several methods of forming contact masses for this reaction have been reported in the literature, which include mixtures of ground silicon and catalysts, alloying of silicon and catalysts together, and sintering of silicon and catalysts (2). The active form of the catalyst in these contact masses has also been the subject of many investigations (3). X-Ray diffraction studies have identified several silicon-copper intermetallic compounds including the γ phase, η phase, and ϵ phase produced during the direct process (3). These Si-Cu compounds may play an important role in the formation of the active sites in this system.

In this report, surface analysis of several contact masses was investigated using X-ray photoelectron spectroscopy (XPS). XPS is a surface sensitive probe for the chemical state of elements present on the surface of a catalyst. Recently, surface chemical studies of the direct process contact masses using XPS have been published by Gupta and Sharma (4). All these studies are with deliberately or inadvertently oxidized surfaces [Chen *et al.* (5) and McLeod *et al.* (6)]. Our studies are different in that the highly reactive contact masses were removed from reactors and analyzed without exposure to the atmosphere. Exposure of these samples to the atmosphere results in severe oxidation. Handling of these samples under inert atmosphere has yielded

results which represent the chemical state of copper during the direct process.

EXPERIMENTAL

The direct process contact masses were obtained from two reactors: a laboratory microreactor and a fluid bed reactor. The samples were removed from the reactors under inert atmosphere conditions, argon, and mounted under the same conditions. The samples, which were finely divided powders, were mounted for surface analysis by embedding in high-purity indium. The contact masses were prepared using two different techniques. In the first one the silicon and copper catalyst were alloyed together and in the second technique the silicon and the copper catalyst were mixed together. Table 1 lists the method of preparation of the contact mass and the reactor used.

Surface analysis was performed on a Perkin-Elmer Model 550 multitechnique, ultrahigh vacuum chamber. The chamber is equipped with a dual-anode X-ray source, magnesium and aluminum, for XPS experiments. Electron energy analysis uses a double-pass cylindrical mirror analyzer. Argon ion bombardment is carried out with a differentially pumped ion gun. The electron

TABLE 1

Method of Preparation of Contact Masses

Sample	Method of preparation	Reactor
A-1	Alloying	Microreactor
A-2	Alloying	Microreactor
A-3	Alloying	Microreactor
A-4	Alloying	Microreactor
M-1	Mixture	Fluid bed

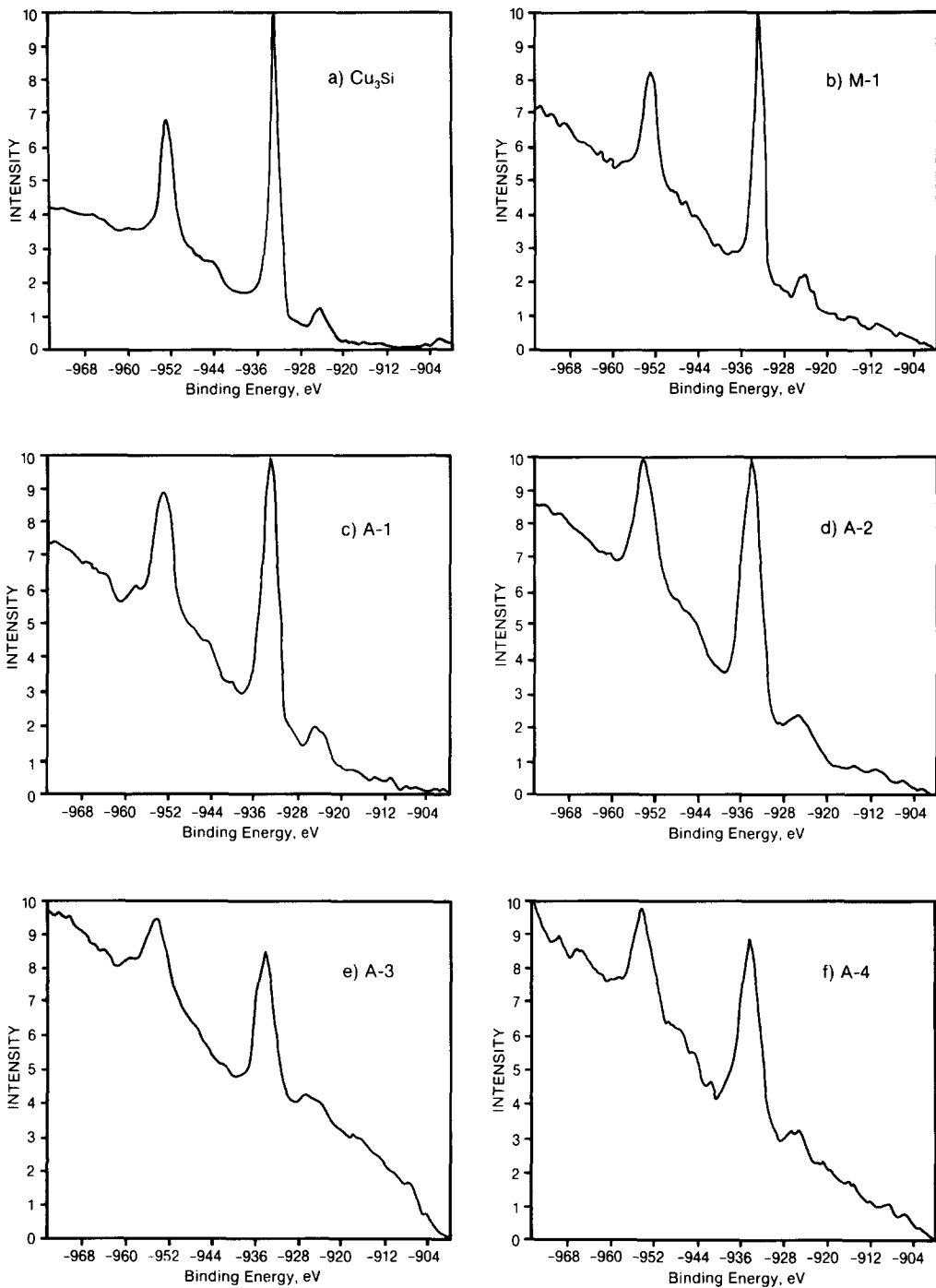


FIG. 1. The XPS spectra for the Cu 2p region for the five contact masses and Cu_3Si are displayed. The energies are uncorrected for changing effects. The spectra are (a) Cu_3Si , (b) M-1, (c) A-1, (d) A-2, (e) A-3, and (f) A-4. The lack of satellite peaks indicate the absence of the Cu^{2+} state.

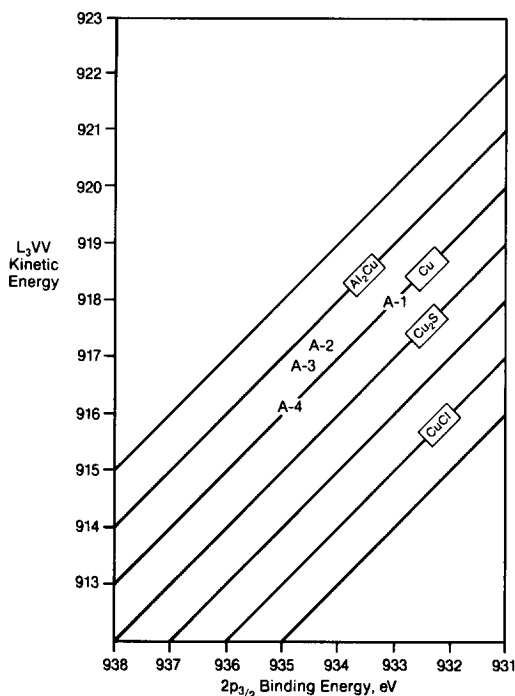


FIG. 2. The data for the four contact masses, A-1, A-2, A-3, and A-4 are plotted on this 2-D scatter plot. The Y-axis is the kinetic energy of the Cu L_{3VV} peak, the X-axis is the binding energy of Cu $2p_{3/2}$ peak, and the diagonal lines are the Auger parameter. All four contact masses fall near the diagonal for the zero oxidation state of copper.

analyzer is interfaced with a Digital PDP11 microcomputer for data acquisition. All spectra were obtained using the Mg anode, a pass energy of 50 eV and sufficient acquisition time to give acceptable signal to noise ratio. All samples were subjected to argon ion bombardment, 5 kV, which removed approximately 30 Å of material.

RESULTS AND DISCUSSION

The X-ray photoelectron spectra of the Cu $2p$ region are shown in Fig. 1 for several contact masses. Also displayed in this figure are the data for a copper silicide, Cu_3Si . A common feature of these spectra is the lack of satellite peaks. Satellite structure on the high energy side of $2p_{3/2}$ is indicative of the Cu^{2+} state (7).

The XPS experiments show that copper is not in the +2 state during the direct pro-

cess. This was found to be true for both methods of preparation of the contact masses. Voorhoeve has observed that contact masses prepared using different techniques gave similar X-ray diffraction patterns, suggesting similar active sites are formed regardless of method of preparation of the contact mass. These results further suggest that copper should be in similar oxidation states in active contact masses (8). The XPS spectra of these contact masses are similar to that of Cu_3Si (see Fig. 1). Our results are in contrast to those of Sharma and Gupta (4). In this study, copper was found to be in the +2 state in direct process samples; however, prior to surface analysis these samples were exposed to the atmosphere. It is highly probable that these samples were oxidized and do not represent the true contact mass during the course of the reaction. The +2 state can be attributed to sample handling procedures, oxidation by exposure of air and not method of preparation of the contact mass. Our results also differ from those of Chen *et al.* (5), who believe copper to be in the +1 state before oxidation.

To further probe the chemical state of copper, the changes in energy of the Cu $2p_{3/2}$ and the Auger L_3VV transitions were analyzed. Wagner has shown that a plot of the kinetic energy of the Cu L_3VV transition versus the binding energy of the Cu $2p_{3/2}$ can distinguish differences in the chemical state of copper in a wide variety of samples (9). Figure 2 shows the data for the contact masses studied in this report. The solid 45-degree lines indicate the same chemical state. Examination of the figure shows copper in these samples is in the same state as elemental copper, the zero oxidation state.

CONCLUSION

The oxidation state of copper in silicon-copper contact masses is zero during the direct process and not the +2 state as previously reported.

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