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EVOLVED GAS ANALYSIS OF COBALT HARDENED GOLD PLATED FILMS

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ABSTRACT

Mass spectrographic evolved gas analysis was performed on Co hardened electrodeposited gold films. Two different rates of deposition were used. The abnormally high rate, 35 mA cm^{-2}, gave rise to a much higher concentration of impurities including relatively large amounts of NH_3, H_2, HCN, and $(CN)_2$ which were evolved around 400°C. Considerably smaller and compositionally different gaseous evolutions occurred near 600 and 800°C. The film deposited at the normal rate, 5 mA cm^{-2}, evolved much less NH_3 and cyanide species and then at somewhat higher temperatures. The major evolution was around 800°C. This indicates that the normally deposited film occluded or codeposited fewer impurities and their higher temperature release probably resulted from the greater continuity of the film.

INTRODUCTION

There has been considerable work on the nature of cobalt hardened gold plated contacts and the deterioration in their electrical and mechanical properties [1—9]. It has been noted that impurities are codeposited which ultimately lead to deleterious effects depending upon time—temperature—atmosphere relationships. These impurities have been investigated by Mössbauer analysis [1,4,6], chemical analysis [5], thermal analysis [9], and transmission electron microscopy [7].

Recent work has shown that films plated at higher current densities show pronounced blistering at elevated temperature [9]. This suggests that even greater impurity concentrations are achieved or that the impurities are of a different nature. This brief paper describes the results of mass spectrographic evolved gas analysis (EGA) of a cobalt hardened gold electrodeposited film prepared at both normal and high current densities.

EXPERIMENTAL PROCEDURES AND RESULTS

Gold films (~11 μm) were electrodeposited from a commercial Sel-Rex CI-Autronex bath. The substrate was 2 mil Pt onto which a 2000 Å layer of Au had been sputtered. The current densities were either 5 or 35 mA cm^{-1} using otherwise standard conditions.

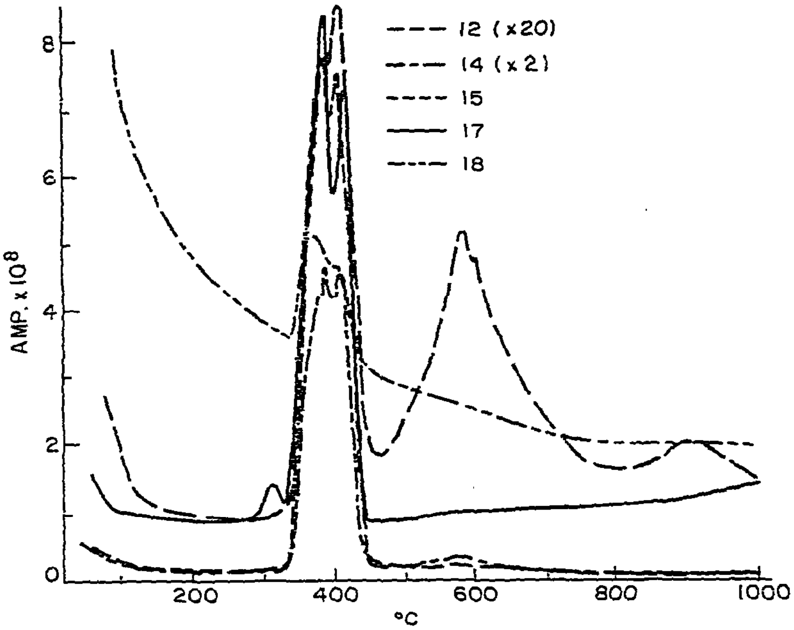

Fig. 1. EGA of 11.7 mg of cobalt hardened gold electrodeposited at 35 mA cm^{-2}. Atomic mass numbers and amplifications are as shown.

The basic EGA apparatus has been described elsewhere [10]. A UTI Model 2054 programmable peak selector was used to program the mass spectrometer and collect the data. A Netzch Model 411 programmer was used to control the sample temperature. A Fluke Model 2190A digital thermometer

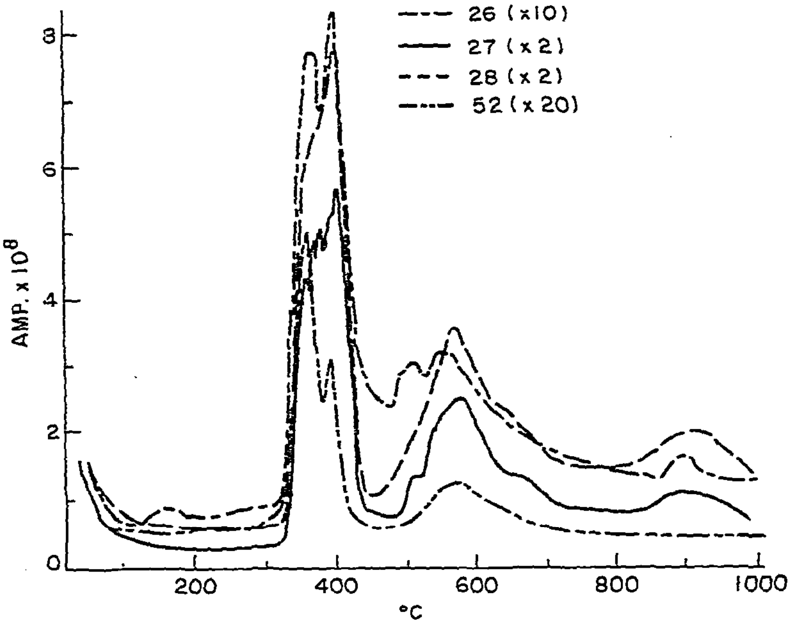

Fig. 2. EGA of 11.7 mg of cobalt hardened gold electrodeposited at 35 mA cm^{-2}. Atomic mass numbers and amplifications are as shown.

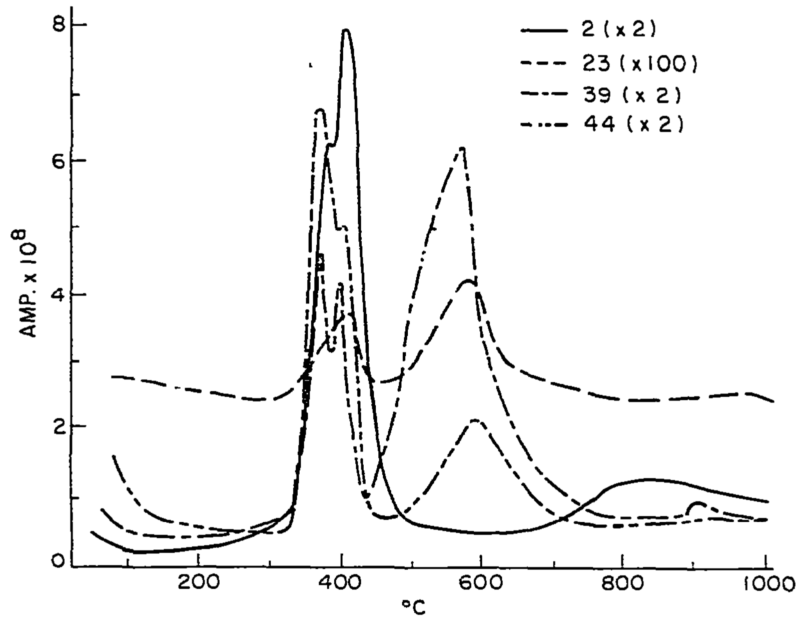

Fig. 3. EGA of 11.7 mg of cobalt hardened gold electrodeposited at 35 mA cm^{-2}. Atomic mass numbers and amplifications are as shown.

coupled with a Spectrum Model 1021 filter/amplifier (10X) was used to supply the temperature input to an analog channel of the programmable peak selector. The heating rate was 10°C min^{-1} and the vacuum ranged from 1×10^{-7} to about 5×10^{-6} torr depending upon the extent of outgassing.

Figures 1—3 summarize the results for the film deposited at 35 mA cm^{-2}

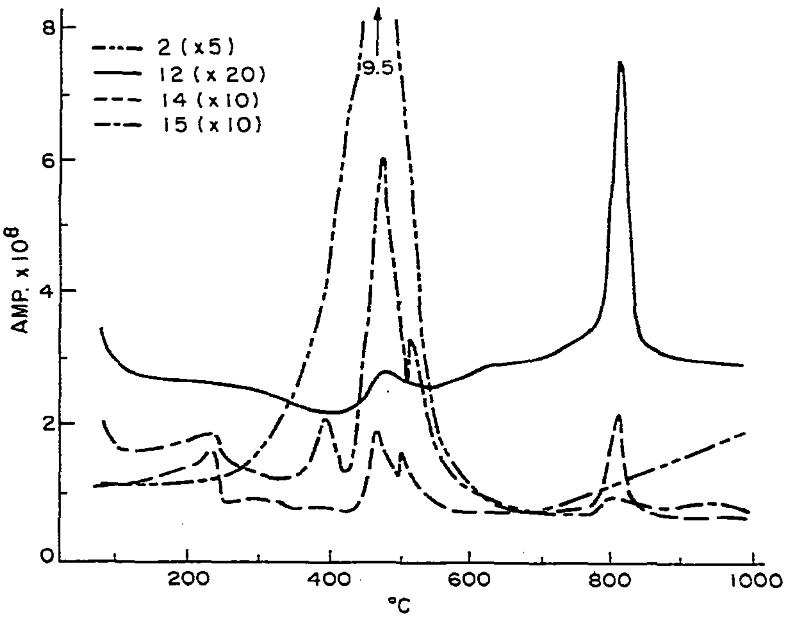

Fig. 4 EGA of 5.7 mg of cobalt hardened gold electrodeposited at 5 mA cm^{-2}. Atomic mass numbers and amplifications are as shown.

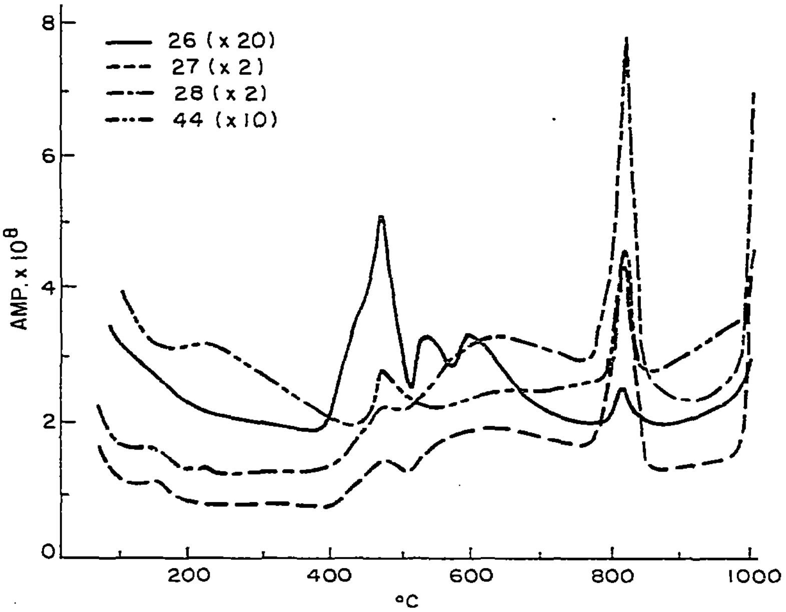

Fig. 5. EGA of 5.7 mg of cobalt hardened gold electrodeposited at 5 mA cm^{-2}. Atomic mass numbers and amplifications are as shown.

and Figs. 4 and 5 are for the film deposited at 5 mA cm^{-2}. In the latter case the curves for masses 17, 18, 23, 39, and 52 were uniformly smooth, typically low level background curves and hence are not reproduced.

DISCUSSION

During the decomposition in vacuum of the rapidly deposited material there are three major zones of evolution. The lowest temperature decomposition around 400°C is the largest. A wide range of products are evolved: NH_3, H_2, HCN, $(CN)_2$, N_2, K, Na, CO_2, and H_2O (see Figs. 1—3). The cyanogen $(CN)_2$, and N_2 are generally products of reduction [11,12]. This is consistent with the known decomposition of such materials as $[Co(NH_3)_6]$-$[Co(CN)_6]$ or $K_3Co(CN)_6$ [13,14]. The presence of H_2O can also form HCN by hydrolytic decomposition. Previous [3] Auger spectroscopy has shown that K (one would also assume Na) migrates to the surface at relatively low temperatures. In general, most of these species can be accounted for by the incorporation of various cyanide complexes or compounds into the gold plate as well as the possible entrapment or occlusion of some bath solution. Hydrogen is frequently incorporated into electrodeposited metals. Since the plating solution does not contain any ammonium salts or ammines, it must be concluded that the NH_3 evolved is either formed during the thermal decomposition by some catalytic mechanism or, more probably, during the electroplating step at high current.

Around 600°C there is a lesser evolution of cyanide species and an increased evolution of the alkali metals. However, there is no evidence for

NH_3 or H_2. This is attributed to the decomposition of the more stable and less volatile cyanides such as $Co(CN)_2$ and the alkali cyanides [13,14]. Finally around 900°C there are much weaker evolutions of CO and cyanide species attributed to the decomposition of any remaining carbides, nitrides, or cyanides [11].

The exact position of these evolutions can also be determined by transformations within the metal films which permit the escape of products, as well as by the equilibrium decomposition temperatures of the bulk products.

The film deposited at the normal current density, 5 mA cm^{-2}, is quite different, as indicated in Figs. 4 and 5. There is much less NH_3 and cyanide species evolved and then only at about 100°C high (500°C). The H_2 evolution is only slightly less but again occurs at the higher temperature. Virtually no cyanogen or alkali metals are observed. Clearly the film has trapped and incorporated far less impurities as would be expected.

There is a slight decomposition of cyanides again around 600°C. The major decomposition now is at the higher temperature around 800°C. The delay to higher temperatures for the decompositions may be due to a greater continuity or protective nature of the film (no blisters).

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