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Prenucleation of Lead Films with Copper, Gold, and Silver

Abstract: Lead films evaporated onto thin nucleating layers of Cu, Ag, and Au were studied by the techniques of electron diffraction and electron microscopy. Electron micrographs indicated that films nucleated with Au become continuous much sooner than films nucleated with Ag or Cu. Examination of the diffraction pattern showed Au to be the only metal of the three to form an intermetallic compound with lead, indicating that compound formation aids in nucleation.

Introduction

The presence of minute quantities of selected surface impurities can dramatically affect the nucleation and growth characteristics of a thin film. For example, by using a nucleating layer of silver several monolayers in thickness, continuous zinc films have been deposited where the probability of the zinc sticking to the substrate would normally be zero.[1] Also a thin (~10 A) nucleating layer of copper has been successfully used in depositing fine-grained tin films on 90 °C substrates. Normally these 5000 A films would consist of agglomerated islands of well oriented (200) crystallites. Other metals, e.g., silver and gold, can be used to produce a similar effect with tin.

At least two possible mechanisms may be responsible for the observations cited above. First, the presence of discrete silver and copper nuclei provides stronger nucleating sites for the arriving film atoms much in the same manner as a cleavage step on an NaCl surface will promote nucleation.[2] The increased binding energy in this case arises from electrical interactions of the nucleating material and arriving metal atoms. Since the density of these nuclei in very thin films of silver and gold is quite high, e.g., $5 \times 10^{11}/\text{cm}^2$ for a 10 A Au film on NaCl, very fine grain films can be deposited. The second mechanism involves intermetallic compound formation, which further increases the binding energy of the film material to the nucleating metal by the heat of formation of the compound. Because the binding energy of a film atom to the substrate enters nucleation theory exponentially,[3] one might expect intermetallic compound formation to have a dramatic effect on the density of critical nuclei present during film growth. The objective of the investigation reported here was to determine the importance of intermetallic compound formation in the selection of prenucleating materials.

Experimental technique

As stated previously, silver, copper, and gold are all effective nucleating agents for tin. However, in bulk material they all form intermetallic compounds with tin.[4] In addition, the presence of Cu_6Sn_5 has been reported in layered structures formed by alternately evaporating thin films of copper and tin.[5] Therefore lead was chosen for the film material because the Pb-Ag and Pb-Cu systems reportedly have no appreciable solubility at either end of the phase diagram (eliminating any contribution to the binding energy from the heat of solution of alloying) and form no intermetallic compounds.[4] In the Pb-Au system there is again no appreciable solubility at room temperature, but the bulk phase diagram indicates the existence of Au_2Pb and $AuPb_2$. By preparing films of these materials and using electron diffraction and microscopy, it was possible to evaluate the importance of intermetallic compound formation in the prenucleation process.

Films were prepared by evaporating high purity metals

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to completion onto NaCl substrates in a glass ultra-high-vacuum system. The substrates were clamped to a copper holder as described by Hoekstra and White[6] and maintained at room temperature by directing a stream of nitrogen gas against the back of the holder. A film of SiO was evaporated onto the NaCl to provide a support for transmission microscopy studies and an amorphous nucleation surface. The prenucleating material was then deposited, followed by the lead evaporation. Finally, the film was covered with a layer of SiO to prevent oxidation.

The average thickness of the nucleating material and the lead film was determined by weighing the material before evaporation and assuming a point source geometry. Absolute values of film thickness may therefore be in error by a factor of two. In an experiment of this type it is important to maintain a fairly constant evaporation rate since the rate at which film atoms strike the substrate enters nucleation theory linearly. This was done by using the same evaporation procedure for each film (identical sources, source heating currents, and evaporation times). Lead evaporation rates were approximately 20 A/sec. Although initial pressures were in the 10^{-9} torr range, the pressure during evaporation of the nucleating material varied between 1×10^{-7} and 5×10^{-7} torr because the weighed material could not be thoroughly outgassed prior to evaporation. During evaporation of Pb, the pressure varied from 1×10^{-7} to 1×10^{-6} torr. Although the total pressure was high during evaporation, mass spectrometer studies have shown this evolved gas to be composed principally of H_2 and CO. These gases do not influence the characteristics of lead films appreciably. The important point is that the partial pressure of critical gases such as O_2 and H_2O was low. After evaporation, the films were floated off the NaCl substrate and examined with a Phillips EM-100 electron microscope. Pictures of the electron diffraction pattern were also taken with a specially designed electron diffraction camera.

To compare pure and prenucleated lead films, shields were placed between the source and the substrate as shown in Fig. 1.

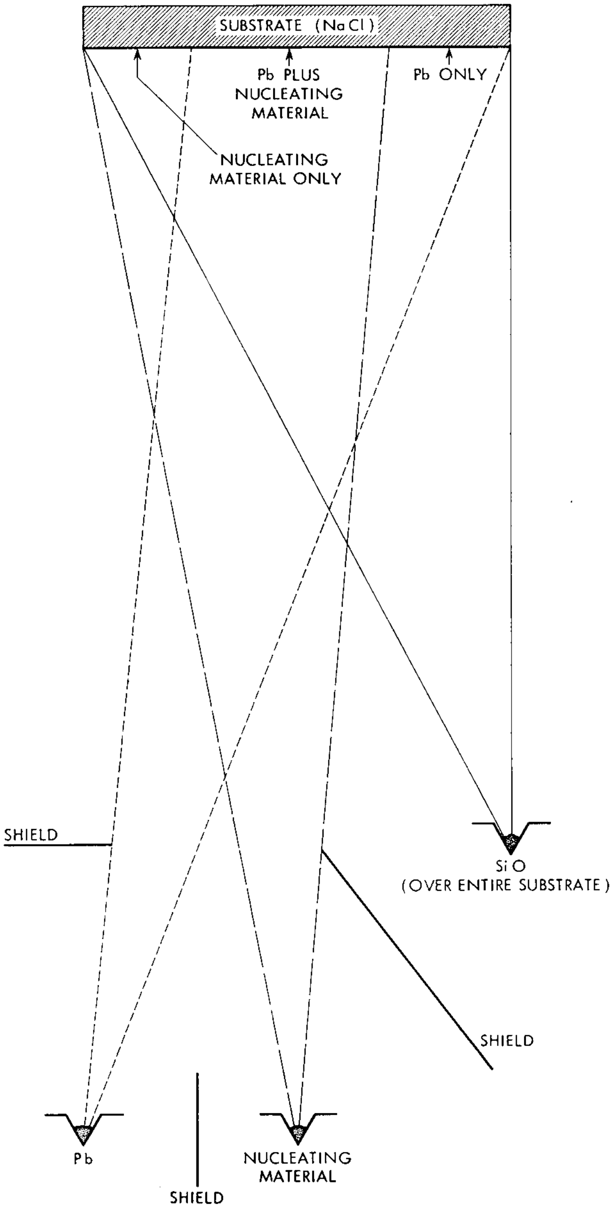


Figure 1 **Diagram of evaporation apparatus.**

Experimental results

Figure 2 is an electron micrograph representative of an unnucleated Pb film. Figures 3, 4, and 5 are electron micrographs of a Pb film deposited on a nucleating layer of Cu, Ag, and Au, respectively. The average thickness of each Pb film and nucleation layer was about 300 A and 10 A, respectively. Differences were detected between each of the nucleated films and the pure Pb film. The grain boundaries of the pure Pb film are quite smooth, and in most cases the grains are not connected. In the nucleated films, almost all of the grains are connected. The big difference, however, is between the Cu or Ag nucleated films and the Au nucleated film. The Cu or Ag nucleated films still have a relatively large amount of open area around each grain, while the Au film is almost entirely continuous.

Figures 6, 7, and 8 show the electron diffraction patterns, and Tables 1, 2, and 3 give the *d* spacings for Cu, Ag, and Au nucleated films, respectively. The electron diffraction patterns in Figs. 6 and 7 are from the same film as Figs. 3 and 4. The film corresponding to Fig. 5 did not have enough alloy present to produce an accurately measurable electron diffraction pattern. Therefore it was necessary to use a film which had more Au. Figure 8 contains the diffraction pattern for a 300 A Pb film nucleated with a 25 A Au film. The electron micrograph of this film was

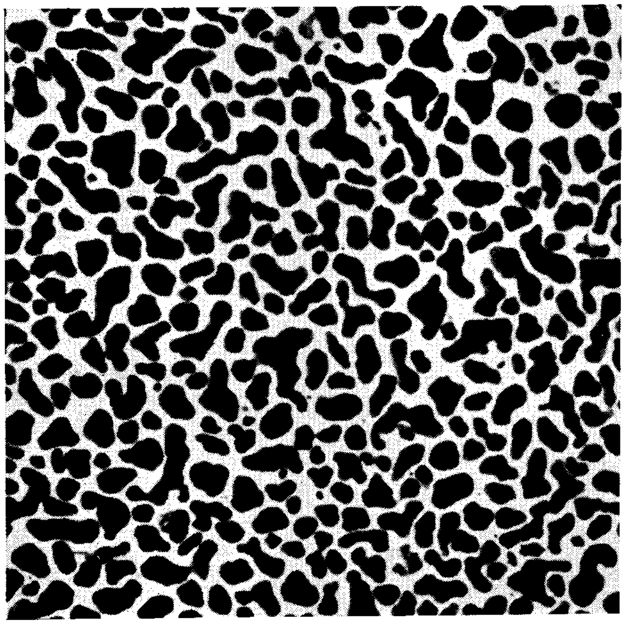


Figure 2 **Electron micrograph of a pure lead film (~300 A). 20,000 ×.**

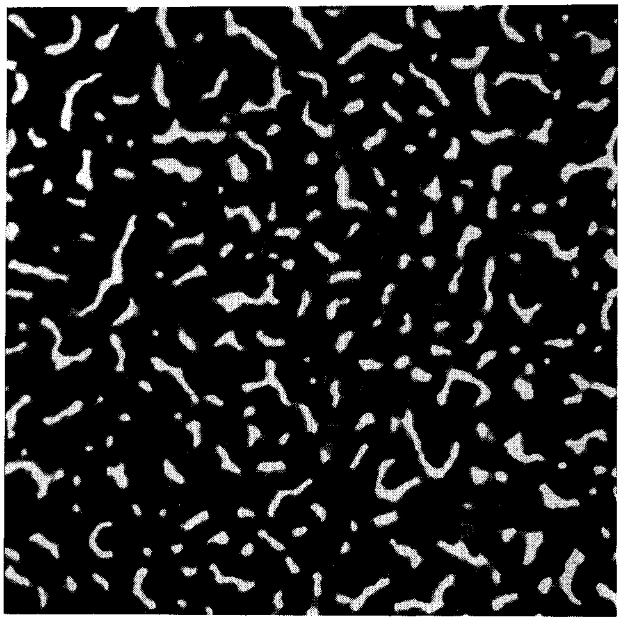


Figure 3 **Electron micrograph of a copper-nucleated lead film.**

Figure 4 **Electron micrograph of a silver-nucleated lead film.**

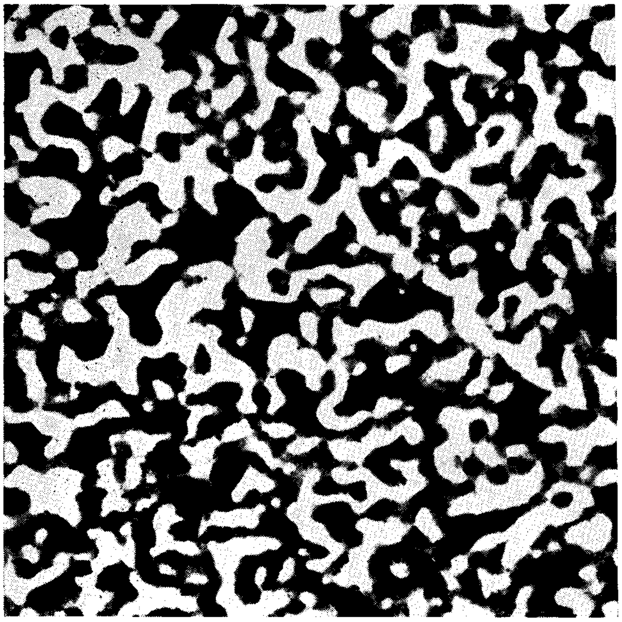
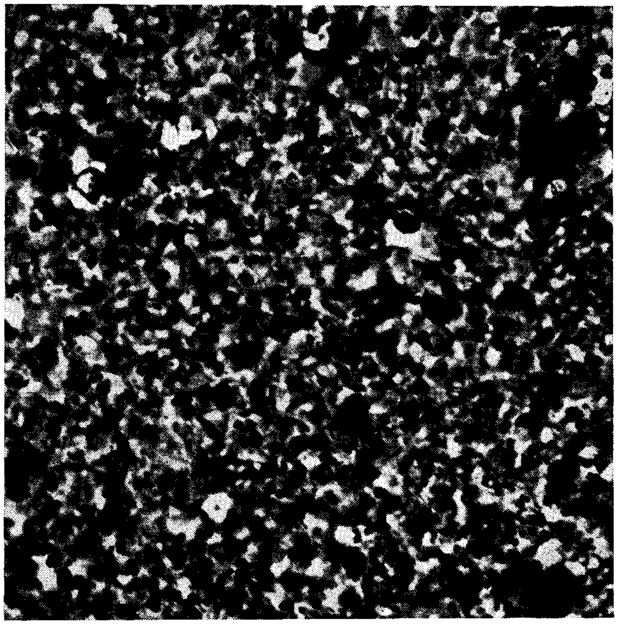


Figure 5 **Electron micrograph of a gold-nucleated lead film.**



similar to that of Fig. 5.

Because the exposure had to be adjusted during printing to reproduce the less intense lines, the relative ring intensities in all the diffraction patterns are not exact. The value listed under d_{calc} is the d spacing obtained from the diffraction pattern by using TlCl as a standard. The d values listed for Pb, Cu, and Ag are those obtained by Swanson and Tatge.[7] The d values for $AuPb_3$ were obtained by Fujiki, Suganuma, and Yoshida.[8] Those listed for $AuPb_2$ were obtained from the X-ray Powder Data File. Only one Cu and only three Ag reflections were observed. The presence of all of the reflections observed by other authors for $AuPb_2$ and $AuPb_3$ could not be clearly demonstrated.

In Fig. 7 there is also one reflection that is not explained. This reflection was observed in a large number of films,

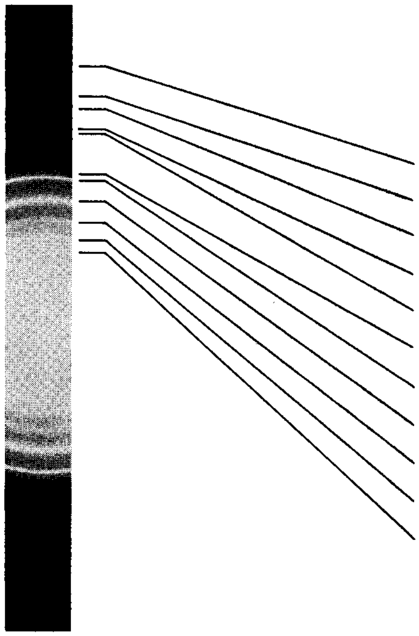


Figure 6 **Electron diffraction pattern for a copper-nucleated lead film.**

Table 1 **d spacing for Cu.**

d_{calc} (A)	Pb		Cu	
	hkl	*d* (A)	*hkl*	*d* (A)
0.838 ±.002	531	0.8369		
0.954 ±.002	511	0.9526		
1.012 ±.002	422	1.0105		
1.110 ±.002	420	1.1069		
1.137 ±.002	331	1.1359		
1.429 ±.004	222	1.429		
1.497 ±.003	311	1.493		
1.752 ±.005	220	1.750		
2.081 ±.008			111	2.088
2.483 ±.008	200	2.475		
2.856 ±.007	111	2.855		

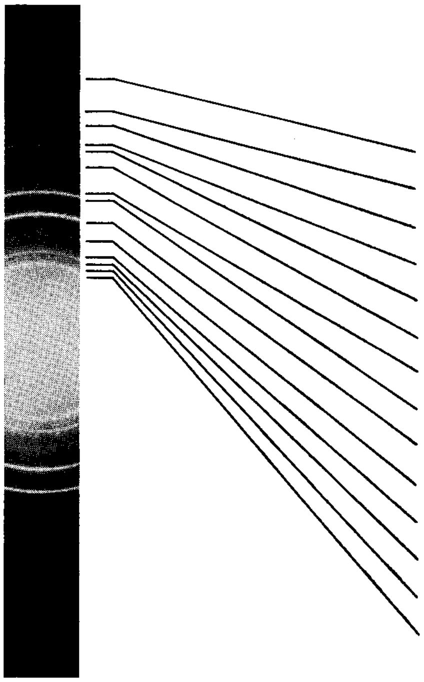


Figure 7 **Electron diffraction pattern for a silver-nucleated lead film.**

Table 2 **d spacing for Ag.**

d_{calc} (A)	Pb		Ag	
	hkl	*d* (A)	*hkl*	*d* (A)
0.833 ±.001	531	0.8369		
0.946 ±.001	511	0.9526		
1.005 ±.001	422	1.0105		
1.101 ±.001	420	1.1069		
1.131 ±.001	331	1.1359		
1.230 ±.001			311	1.231
1.424 ±.001	222	1.429		
1.485 ±.001	311	1.493		
1.742 ±.002	220	1.750		
2.071 ±.007			200	2.044
2.356 ±.006			111	2.359
2.464 ±.003	200	2.475		
2.617 ±.002				
2.840 ±.003	111	2.855		

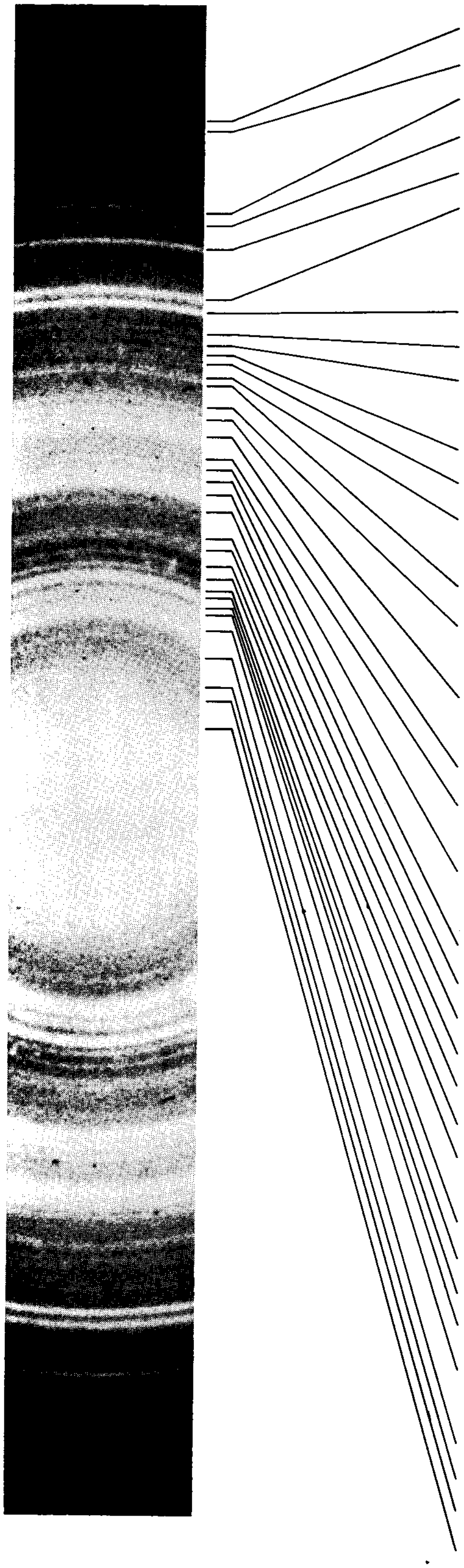


Figure 8 **Electron diffraction pattern for a gold-nucleated lead film.**

Table 3 **d spacing for Au.**

d_{calc} (A)	Pb *hkl*	Pb *d* (A)	$AuPb_2$ *hkl*	$AuPb_2$ *d* (A)	$AuPb_3$ *hkl*	$AuPb_3$ *d* (A)
0.825 ± .002	600	0.8251				
0.837 ± .002	531	0.8369				
0.953 ± .002	511	0.9526				
0.980 ± .002						
1.012 ± .002	422	1.0105				
1.108 ± .003			541			
	420	1.1069	602	1.111		
			404			
1.136 ± .003	331	1.1359				
1.189 ± .003						
1.212 ± .003			314	1.205	444	1.206
			600	1.219	653	
1.243 ± .003	400	1.238	224	1.238	851	1.239
1.264 ± .004			530	1.257		
1.297 ± .003			440	1.294	901	1.296
			413			
1.313 ± .004			521	1.322	414	1.311
1.396 ± .003					613	1.388
					224	
1.434 ± .007	222	1.429	510	1.435	741	1.438
					811	
1.491 ± .004	311	1.493	332	1.470		
1.583 ± .004			402	1.535	542	1.576
					721	1.582
1.633 ± .004			420	1.632	711	1.625
			213		602	1.650
1.695 ± .004			411	1.693	710	1.691
1.750 ± .004	220	1.750	330	1.727		
1.962 ± .007					611	1.864
2.036 ± .007					521	2.077
2.092 ± .006					402	2.096
2.223 ± .007			202	2.236	520	2.221
2.336 ± .006			310	2.310	312	2.321
					510	2.345
2.432 ± .007					222	2.413
2.481 ± .005	200	2.475	112	2.477		
2.607 ± .008			220	2.59	411	2.600
2.664 ± .007					420	2.674
2.851 ± .009	111	2.855	211	2.84	330	2.818
			002		321	2.888
3.301 ± .007					301	3.229
3.953 ± .011					211	3.956
4.234 ± .022					220	4.224
5.294 ± .020					101	5.295

not all of which were Ag nucleated films. For example, close observation of Fig. 8 shows spots in approximately the same position as the "extra" reflection. Other extra reflections were observed in several films. For example, in one film reflections corresponding to *d* spacings of 3.81, 2.23, 2.00, 1.64, and 1.09 A were obtained. This film had been evaporated under vacuum conditions that were poorer than usual. In another Ag nucleated film, reflections corresponding to *d* spacings of 3.33, 3.03, 2.23, 1.96, and 1.69 A were observed. This film had been in the electron diffraction camera for several days before it was examined. Although the exact cause of these extra reflections is not known, they are believed to be produced from some reaction product of Pb. In support of this, it can be noted that some of these reflections were obtained in films which were not prepared in the ultra-high-vacuum system and which were nucleated with materials other than Ag.

Discussion

This investigation has shown that a lead film, nucleated by a very thin metal layer containing a high density of nuclei, will become continuous much sooner than an unnucleated film. Also, films nucleated with Au become continuous much sooner than films nucleated with Ag or Cu. Although it is not possible to state conclusively that the ability to form an intermetallic compound is a requirement of a good nucleating material, our results indicate that the formation of such compounds is important in the nucleating process.

This work also clearly illustrates the importance of substrate cleanliness. For example, the improved adhesion and increased reflectivity obtained through glow discharge substrate cleaning may in many instances be due to small quantities of sputtered material rather than to cleaner substrates. Extreme care is required in ion cleaning if minute quantities of contaminants are to be avoided.

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