Controlled Electron Beam Co-deposition of Copper-Nickel Films*

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The effect of process variables in controlled co-deposition of copper-nickel films employing one oscillated electron beam and two pure sources was systematically studied. Structural features were investigated by optical microscopy and X-ray and electron beam analysis. Correlations between structure and growth conditions were sought.

The effect of substrate temperature was found to be similar to that observed in single element deposition: Grain size increased with temperature and preferred orientation appeared above 300° C. At high frequencies of electron beam oscillation a homogeneous binary vapour appears to be formed and deposited similarly to a single component vapour. Films co-deposited at low frequencies exhibited topographies suggesting periodic rather than simultaneous deposition of two vapours.

Controlled and reproducible co-deposition was confined to experimental limits due to the use of equal area sources. It is believed that the difference in thermal properties of the source materials leading to the above limitation, can be compensated for by evaporation from sources of different surface areas.

1. Introduction

Thin film science and technology has been experiencing very rapid growth in recent years. In spite of, or perhaps because of, this rapid growth, some basic problems in thin film technology have not yet been satisfactorily resolved. One of these is the problem of controlled and reproducible deposition of multi-elemental films.

Many workers, mainly in industry, were faced with some modification of this basic problem. The present state of incomplete understanding and mastery of materially complex film deposition processes may be partly blamed on non-systematic attempts at solution. Most of the research has so far been conducted in response to some specific practical demands. Too little work has been performed in a strictly academic environment where the investigator is free to develop his own tools and techniques. Even more important: where he can decide for himself what material systems suit best his research purposes without immediate interference of commercial aspects. We report here results of unsponsored research which has been carried out under such favourable conditions.

Simultaneous electron beam evaporation from separate metal sources appeared to be a promising solution to the problem of controlled and reproducible deposition of alloy films. The method, which we describe in greater detail elsewhere [1], employs one electron beam generated by a self accelerated gun and oscillated in a controlled manner between two evaporation sources. The dwelling time of the beam on each source determines the evaporation rates of the individual constituents. Composition of films is controlled by varying the ratio of dwelling times. The geometry of deposition was designed to produce films of uniform thickness and composition.

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After determining the applicability of this method to various material systems it was decided to evaluate it more basically by a systematic study of the co-deposition process variables. The copper-nickel system was chosen for this purpose because of its inherent simplicity. As is well known, the copper-nickel system displays complete miscibility and, therefore, enables a study of the process over the whole range of compositions. The effect of process variables on growth-structure relationships was mainly investigated.

2. Experimental Procedures

2.1. Preparation

Throughout the course of work equal geometrical conditions of evaporation were maintained for the two sources. High purity materials were used not only in order to facilitate analysis of results, but mainly to prevent evolution of dissolved gases during evaporation. Both sources were accurately cut to 5 mm in diameter by 5 mm long cylinders from spectrographically pure copper and nickel rods (Johnson, Matthey and Co, Ltd). The cylinders were then etched to eliminate any surface contamination which may have occurred during machining. They were thereafter introduced into 5.1 mm in diameter by 2 mm deep holes, each drilled in a separate graphite crucible [1].

All substrates used in the presently reported experiments consisted of optically flat $0.002 \times \frac{7}{8} \times 1\frac{1}{8}$ in. cleaved muscovite mica crystals. The substrate assembly provided control and accurate recording of temperature over a wide range ($-200°$ C to $500°$ C).

After reaching a pressure of 5×10^{-5} mm Hg or lower in the vacuum chamber, and adjusting the substrate temperature to a predetermined value by heating or cooling, the electron beam was turned on. The desired settings of beam voltage, current, and focusing were applied, and the proper dwelling times introduced to the deflection magnet. Deposition was not started before reaching stable conditions.

Five main variables of the co-deposition process were studied: (1) ratio between dwelling times of the beam on both sources; (2) frequency of beam oscillation (which is equal to the reciprocal of the sum of the dwelling times); (3) electron beam power; (4) electron beam voltage-current combination for a given power setting, and (5) temperature of the substrate.

All parameters, except for the studied variable, were kept constant in a given series of experiments.

2.2. Examination

Thickness and composition of deposited films were determined by X-ray fluorescence using standard curves obtained by calibration with accurate but destructive chemical colorimetry and multibeam interferometry techniques. Several readings, each of a small area in different parts of the substrate, were taken in order to detect any variations in composition. Finer scanning of the surface of several films was performed using an electron microprobe X-ray analyser.

Conventional light microscopy was used to investigate topographical features. Electron microscopy revealed considerably more details. Replication was required since all films of this study were too thick for transmission.

An attempt has been made to use X-ray diffraction methods for the determination of preferred orientation, grain size and other structural features. However, single crystalline mica reflections were too intense, obscuring all other lines. It was then decided to employ electron diffraction techniques. Since the films were too thick for transmission, the reflection or grazing incidence method was used.

3. Results

Altogether some fifty copper-nickel films were grown, ranging in thickness from about 0.1 to 2.2 μm (1000 Å to 22 000 Å). The range of deposition rates was from about 3 to 175 Å/sec. Composition varied from 4.6 to 98.5 wt % copper. Scanning by X-ray fluorescence and in the electron microprobe analyser revealed no meaningful changes in thickness or composition over the surface of a given film.

Individual series of experiments will now be separately considered.

3.1. Dwelling Times Ratio

Although the controlled oscillation unit was capable of providing any dwelling times ratio between 1:100 and 100:1, it has become evident during the preliminary experimentation period that the practical region is much smaller. The limiting ratios are those at which one metal source is evaporating at very high and hardly controllable rates while the other is scarcely molten. In the case of copper-nickel heated by a 1.2 kW (8 kV by 150 mA) electron beam, the

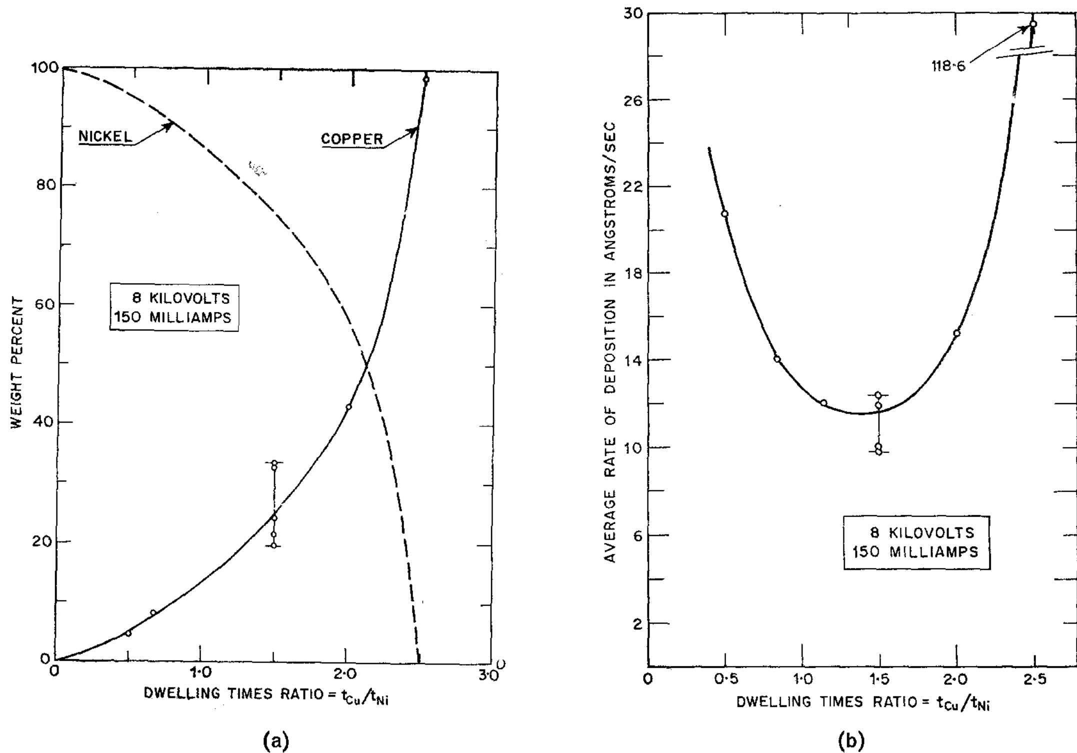

Figure 1 Effect of dwelling times ratio on (a) composition, and (b) rate of evaporation of copper-nickel films.

limits were found to be: $(t_{Cu}/t_{Ni})_{max} = 2.5$, and $(t_{Cu}/t_{Ni})_{min} = 0.5$.

Experiments were performed at six different ratios within the above limits. One of the dwelling times was always kept at the instrumental minimum of 600 μsec, thus attaining the highest possible frequency of oscillation in each case. The substrate holder was neither cooled nor heated during deposition; substrate temperatures due to source radiation never exceeded 120° C.

Composition of films thus obtained is plotted as a function of dwelling times ratio in fig. 1a. The average rate of deposition is plotted as a function of dwelling times ratio in fig. 1b. The spread of points at $(t_{Cu}/t_{Ni}) = 1.5$ is a result of additional values from experiments performed under similar conditions in other series.

3.2. Frequency of Oscillation

In this series of experiments the electron beam power was kept at the same level as in the previous experiments (8 kV $\times$ 150 mA = 1.2 kW). Neither was the substrate temperature changed. The ratio of dwelling times was constant at $t_{Cu}/t_{Ni} = 3/2$, but their lengths were varied covering a range of frequencies from 33.3 to 666.6 cps.

The results have shown a slight, almost linear increase in the rate of deposition with the decrease in frequency of oscillation. No considerable variation in thickness or composition has been detected by X-ray fluorescence or electron microprobe scanning analysis. Structural effects were detected as shown in fig. 2. A definite coarsening and development of crystalline facets is observed as the frequency of oscillation is lowered.

3.3. Electron Beam Power

This and the next series of experiments deal with variables related to the electron beam voltage and current settings. Any variation in either one of these settings introduces a change in the electron beam power. A systematic way had to be used, therefore, in order to differentiate between the effect of power variation and possible effects of current-voltage combination. It has been decided to keep the voltage constant and vary the current covering all the range of power values provided by the high voltage supply.

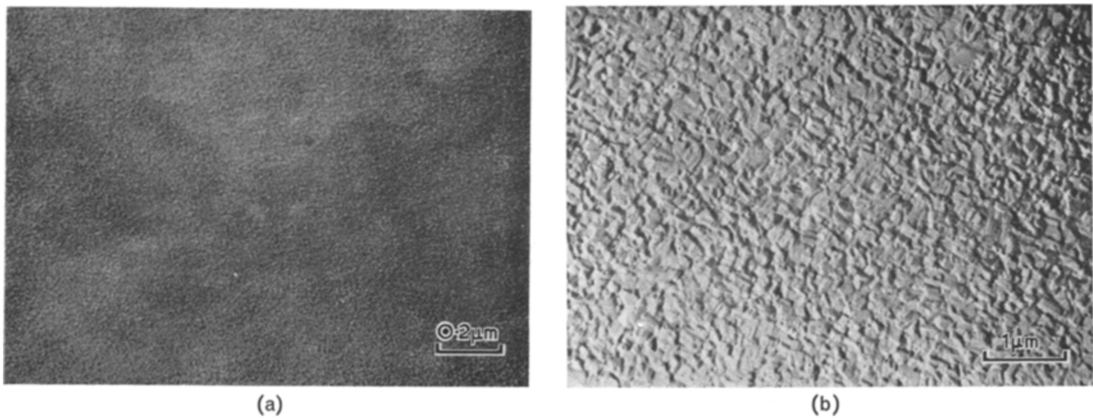

Figure 2 Electron micrographs (replication) showing the effect of frequency of oscillation on topography of copper-nickel films: (a) at 333.3 cps (× 24 000), and (b) at 33.3 cps (×6 000), exhibiting crystalline facets on surface of film.

The dwelling times ratio was $t_{Cu}/t_{Ni} = 900/600$ µsec in all experiments. The substrate temperature was not controlled and the beam voltage was kept at 8 kV. The current was varied in the range of 125 to 250 mA; the limits being set by the lowest and highest possible rates of evaporation. The rate of deposition as a function of power between 1.0 and 2.0 kW is plotted in fig. 3a. The wt % of copper in the films was constantly rising with the increase in power, from 18.2% at 1.0 kW to 87% at 2.0 kW. Considering this rise, separate rates of deposition for copper

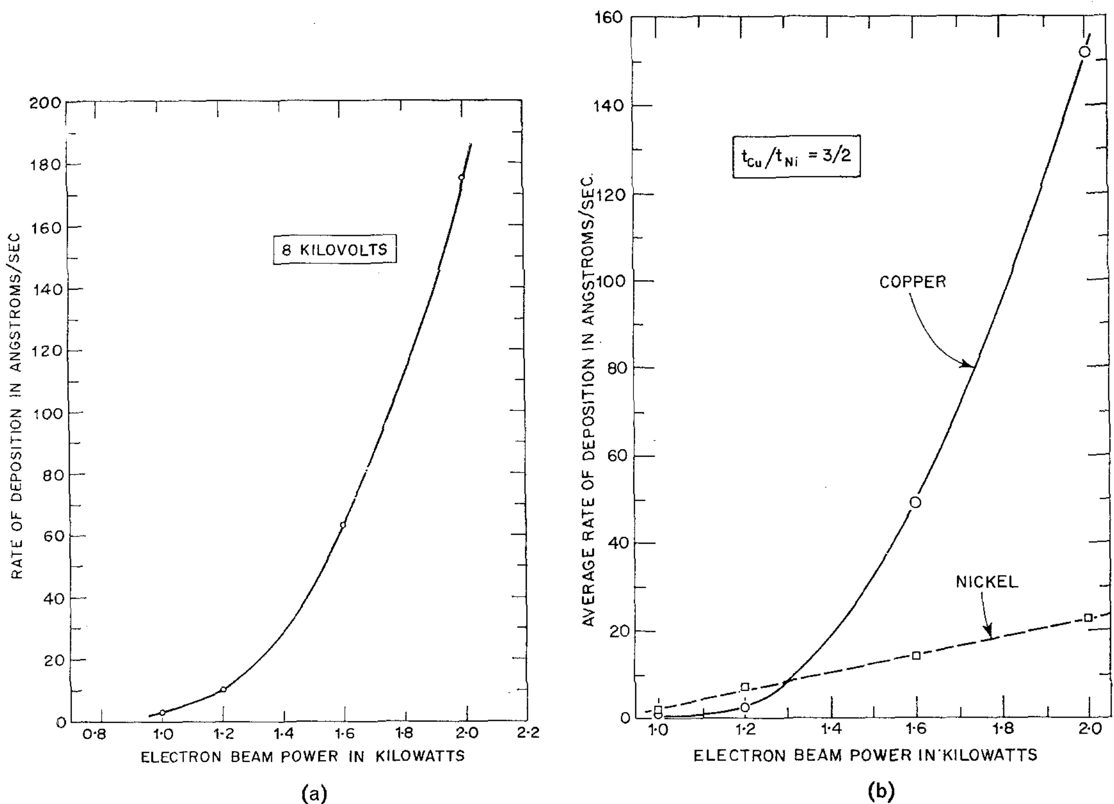

Figure 3 Effect of electron beam power on (a) total, and (b) individual rates of deposition of copper and nickel.

and nickel were calculated and plotted as a function of the power input. The resulting curves are shown in fig. 3b.

3.4. Electron Beam Voltage-Current Combination

The power in this series of experiments was kept constant at the value of 1.2 kW. The voltage-current combination was changed, however, as follows: 10 kV × 120 mA, 8 kV × 120 mA, 6 kV × 200 mA and 5 kV × 240 mA.

No meaningful variations in the rate of deposition or composition were observed. The only noteworthy observation of this series was perhaps the fact that ionization was more pronounced at the higher current settings. This was evidenced by discharge sparks and violet light radiation originating above the sources. The increased ionization seemed to cause coarsening of film surfaces.

3.5. Substrate Temperature

This was the only series in which the temperature of the substrate holder was controlled by heating or cooling. It was revealed that substrate temperatures rise rapidly at the start of deposition. They continue to climb steadily, but at a slower rate, reaching, at the end of deposition, values of about 100° C above that of the holder. Cooling is relatively gradual after the first sudden drop following beam shut-off.

The electron beam power was always kept at 1.2 kW (8 kV × 150 mA), and the dwelling times ratio was usually $t_{Cu}/t_{Ni} = 900/600$ μ/sec. No meaningful variations in the rate of deposition or composition were recorded in seven experiments employing different substrate temperatures in the range of − 200° C to 450° C.

Reflection electron diffraction patterns taken of all films in this series revealed a gradual increase in grain size consistent with microscopical findings. The diffraction pattern of a film deposited under liquid nitrogen cooling conditions exhibited weak, diffuse rings implying very fine grain size if not amorphism. Preferred orientation was detected in films deposited at temperatures higher than 300° C.

4. Discussion

A basic parameter in any vacuum deposition process is the power input to evaporation sources. Two variables were unique in the present co-deposition process; the dwelling times ratio and the frequency of oscillation. However, even these specific parameters can be expressed in terms of power input. A thorough examination of the power factor should, therefore, first be attempted.

Crawford [2] employed a semi-quantitative approach to the problem of input power disposition. He showed that the most important factor is surface temperature of the source, since it determines the rate of evaporation as well as the major heat loss: conduction. Theoretical calculation of surface temperatures of a source changing in geometry and heated by a pulsed electron beam is very difficult, if not impossible. Accurate experimental measurement of surface temperatures of molten metals is practically prohibitive. In fact, the most reliable method to produce meaningful temperature readings of evaporating metal surfaces is perhaps one based on calculations performed on experimentally measured rates of evaporation [3]. Thus, only qualitative considerations will be used here to explain the experimental results presented above.

Fig. 3a implies that the rate of evaporation increased parabolically with increasing power input. It becomes evident from fig. 3b that the parabolic increase is actually due only to copper, since the rise in rate of deposition of nickel is nearly linear. Fig. 3b is, however, somewhat misleading. Due to the dwelling times ratio, the input power is varied over different ranges for each metal.

In the case of nickel, the range was 400 to 800 W, while for copper it was 600 to 1200 W. In the overlapping power region, nickel evaporates even faster than copper, which exhibits an abrupt rise in rate of evaporation only above 800 W.

A possible explanation of this phenomenon may be found in the difference of physical properties, mainly heat conductivities and melting points, between the two metals: $K_{Cu} = 0.941$, $K_{Ni} = 0.22$ cgs units; $T_{mCu} = 1083°$ C, $T_{mNi} = 1455°$ C. When the power input is relatively low, causing a small amount of superheating, conduction losses will be higher for copper due to the higher conductivity, K. Consequently, at such power levels, nickel will tend to display higher rates of evaporation due to better heating efficiency. With increasing power inputs, even a small rise in superheating will considerably increase the rate of evaporation which is proportional to $T^{-0.5}$ [4]. At the same time, the temperature gradient, and hence conduction in copper will not change much because of the levelling

effect of a high K value. Conduction in nickel will increase relatively more because of the build-up of temperature gradients favoured by a lower K value. This will lead in copper to a progressively increasing amount of power used up directly for evaporation, while in nickel, conduction and evaporation will still be rising in parallel and cause only a linear increase in evaporation rate with power input. Consideration of radiation losses which are proportional to T^4 and, therefore, much higher for nickel, aids in explaining this trend.

It must be stressed that the above reasoning is applicable to nickel only for relatively low power inputs. Nickel will probably, by the same mechanism as copper, also exhibit a sudden rise in evaporation rate. However, this can happen only at input powers higher than those used in the present investigation. Indeed, a curve obtained by MacDonald [5] shows a sharp rise in the rate of deposition of nickel-chrome films when power inputs reached values higher than 1.5 kW.

Whatever the explanation of the power effect, it in itself explains the effect of the dwelling times ratio (fig. 1). Expressing the variation of conditions in terms of input power, the effect on the composition and rate of deposition can be understood. As long as the power input to the copper source is kept at values lower than about 900 W, nickel will evaporate more readily, leading to nickel rich alloy films and relatively low rates of deposition. When dwelling times ratios which result in input powers exceeding the above value for copper are used, an immediate and sharp increase in the rate of copper evaporation occurs. This is expressed by an increased rate of overall deposition and by a sharp rise in copper concentration, as was indeed observed. At low copper and high nickel input powers, the increase in percentage of nickel and the rise in overall rate of deposition will be evident, but not as sharp as in the other case.

A region of minimum deposition rate for relatively nickel-rich films can be predicted. This is confirmed by the experimental curve of fig. 1b. The region will also be one where control of thickness and composition can be more easily achieved, since small variations or inaccuracies in the power input and dwelling times ratio will not result in sharp changes in deposition rates of the two metals. On the other hand, the rate of evaporation in this region is relatively lower.

The lack of any significant effect of the voltage-current combination, can be attributed to the fact that voltage was varied over a rather narrow range which did not cause any serious change in depth of electron beam penetration. This depth can be calculated [6] as a function of acceleration voltage and in this case (5 to 10 kV) it is found to be of the order of 1 μm for both metals.

The slight linear increase in deposition rates with decreasing frequencies of oscillation, can be most simply explained by the decreasing loss of input power occurring when the electron beam is in transit between the two sources. The oscillating magnetic field is not an ideal square wave, since a time constant is introduced by instrumentation. At higher frequencies, a larger percentage of the overall time and power will, therefore, be lost on switching from source to source. However, one can expect that at considerably higher frequencies and for more closely square waves, the rms rate of evaporation will increase even above the value obtainable from a source continuously bombarded by a beam of equal energy. This was shown [2] to be due to the fact that higher rms source surface temperatures are reached with oscillating beams. Since the rate of evaporation is proportional to $T^{-0.5}$ [4], it is very sensitive even to small changes in surface temperature. Pulsed rather than continuous beams are, for this reason, used in high power electron machining applications.

Although no compositional inhomogeneity was microscopically detected in the case of films deposited under low frequencies of oscillation, the electron micrograph of fig. 2b may imply that the film is made up of some segregated crystallites. In contrast with fig. 2a, which is an electron micrograph of a film deposited at high frequencies of oscillation, fig. 2b shows some well developed crystalline facets and relatively large grains, although thermal conditions of deposition were equal in both cases. A possible explanation of the phenomenon may be as follows.

The dwelling times at the low frequency are sufficiently long (of the order of 10^{-2} sec) for one source to cool off considerably and almost stop evaporating while the beam dwells on the other source. This has actually been observed by the flickering in brightness of sources during deposition. It is, therefore, impossible to speak here of a simultaneous co-deposition process, because it resembles more a process of periodic deposition of consecutive layers of two metals. Consider the second part of the first deposition period. Metal

B is being deposited not on a clean substrate, but on one which already has nuclei of A, deposited during the first part of the period. If the dwelling times were long enough to obtain a complete layer of metal A, it is doubted whether any special structural effect could be finally observed. But as it is, only islands of A are present on the substrate, forming sites of preferred nucleation for the deposition of metal B. The first several periods are important in establishing a pattern of preferred nucleation which will eventually develop into growth of large crystallites with well developed facets.

The above reasoning could also be carried out in terms of "growth poisoning" which has recently become a widely used concept in considering growth-structure relationships. In this case, metal A would be considered to be a contaminant rather than an alloying element in the deposition of B during the second part of the first period. The role of impurities is known to be of importance in the nucleation [7], as well as in the growth stage [8]. Final topographies exhibiting macroscopic steps and crystalline facets can often be traced back to impurity adsorption. Several reports have particularly stressed the important role of contamination in epitaxial film growth [9-11]. At frequencies of oscillation of the order of magnitude of 100 cps or higher, evaporation from either one of the sources will never stop completely, although the rate may change periodically. It can be concluded, that whenever two soluble metals are co-deposited at such high frequencies, they behave as if the alloying was taking place in the vapour phase, leading to condensation of a homogeneous binary vapour and forming a single phase film. If a lapse of time is introduced (at the low frequencies) preventing the "mixture" or "alloying" of the two metal vapours, and the temperature of the substrate is not high enough for homogenisation to occur by surface diffusion, a poisoning effect is observed, even in the case of periodic deposition of miscible metals.

Results of experiments performed in the substrate temperature series conform to the above pattern. Grain size was larger at higher temperatures and preferred orientation was observed above 300° C. Complete epitaxy has not been achieved because heating of mica substrates was limited to 450° C. The vapour deposited at the substrate appears to behave like a homogeneous binary phase. Nucleation and growth did not introduce any compositional segregation.

5. Conclusions

In summary, it can be concluded that controlled and, to some extent, reproducible co-deposition of copper-nickel films using a 1.2 kW electron beam oscillated at frequencies higher than 100 cps between equal area sources, is practically confined by the following experimental limits: dwelling times ratio, $t_{Cu}/t_{Ni} = 0.5$ to 2.0; rate of deposition = 10 to 15 Å/sec; composition = 5 to 40% copper.

The above limits in composition and rate of deposition can, however, easily be extended by a change in the geometry of deposition, especially by adjusting the surface areas of sources.

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References

1. M. ORON and C. M. ADAMS, JR, submitted for publication in the *J. Sci. Instr.* **2** (1969).
2. C. K. CRAWFORD, "Introduction to Electron Beam Technology" edited by R. Bakish (Wiley, London, 1962) p. 315.
3. *Idem, ibid*, p. 331
4. I. LANGMUIR, *Phys. Rev.* **2** (1913) 329.
5. W. J. MACDONALD, "Proc. 4th Symp. on Electron Beam Techn". (Alloyd, 1962) p. 342.
6. L. KATZ and A. S. PENFOLD, *Rev. Mod. Phys.* **24** (1952) 28.
7. J. P. HIRTH and G. M. POUND, "Condensation and Evaporation, Nucleation and Growth Kinetics" (Macmillan, London, 1963) p. 56.
8. *Idem, ibid*, p. 112 and p. 130.
9. S. INO, D. WATANABE, and S. OGAWA, *J. Phys. Soc. Japan* **17** (1962) 1074.
10. S. SHINOZAKI and H. SATO, *J. Appl. Phys.* **36** (1965) 2320.
11. J. W. MATHEWS and E. GRUNBAUM, *Appl. Phys. Lett.* **5** (1964) 106.