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Interface epitaxy and self-epitaxy of metals near room temperatures

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The recently developed technique of metal-metal epitaxy on silicon (MMES) allows a number of metals to be epitaxially grown without an intentional heating of the substrates. Using (100) Cu epitaxially grown on (100) Si as the seed, or other metals on Cu as the seed, growth of (100)-oriented films has been obtained for fourteen metals, at a thickness of 1000 Å, including both face-centered cubic (fcc) and body-centered cubic (bcc) metals. Two determining factors involved in such a growth are discussed: an interface heteroepitaxy, followed by a self-epitaxy of the metals. The role of lattice match in the interface epitaxy is illustrated by the growth of (100)-W and (100)-Nb films, both bcc metals, on the differently matched metal seed layers. A rotation of 45° between the (100)-bcc metal grown and the (100)-fcc seed layer is suggested and confirmed. The epitaxial growth of these metals further allows a comparison of the substrate temperature used with the melting temperatures of the metals. The ratio of the substrate temperature to the melting temperature of the metals grown by the MMES technique ranges from 0.24 for Ag to 0.08 for W, using 300 K for the substrate. It is suggested that the technique be used to determine consistently the minimal substrate temperatures needed for the epitaxy of these metals, allowing a fundamental understanding of the epitaxial growth of metal films.

Thin-film growth has been a fascinating area for science, and is of vital importance to technologies. Most work has been on metals and semiconductors.[1-6] The film properties and qualities are often sensitive to the growth conditions. Of special interests are the conditions for an initiation of epitaxy at the interface, and the minimal temperatures needed for the growth of single-crystal or epitaxial films. Lattice matching has often been accepted as a prime factor for the former, while temperatures about one-half to one-third of the melting points of the materials have often been mentioned for the latter.[1-3]

Recently, we have reported the epitaxial growth of (100) Cu on (100) Si.[7] Using grazing-angle-diffraction analysis, the (100) Cu is found to rotate 45° around its [001] axis relative to the Si(100) lattice for an improved lattice matching. Cu thus shows an in-plane epitaxial relation with the Si substrate, with Cu[110] parallel to Si[100].[8] Furthermore, the channeling analysis of a 2-μm (100)-Cu film thus deposited shows a low dechanneling yield of 10% near the surface.[8] It is then interesting to use the (100)-Cu film as a seed for the growth of other metals in this orientation, achieving metal-metal epitaxy on silicon (MMES). On the Cu seed, we have observed the (100) growth of several face-centered cubic (fcc) metals, Ni, Co, Rh, Ir, and Pd.[9,10] The MMES technique has also allowed the growth of (100)-oriented periodic structures of Ni-Cu, Co-Cu, and Ni-Co.[10] The fcc metals, normally grown in the (111) orientation, are shown to grow in the (100) orientation using the (100) Cu/Si substrates. Other fcc metals, which do not grow epitaxially on Cu due to the large lattice mismatch, can be grown in the (100) orientation using an additional metal layer on Cu to provide the needed lattice match. Examples include the growth of (100) Au, Ag, and Pt on the (100) Pd deposited on Cu.[9] The metal films grown, in turn, allow a further epitaxial growth of other metals, including the body-centered cubic (bcc) metals in the (100) orientation, which are otherwise grown in the (110) orientation.[9] To date, fifteen metals have been grown in the (100) orientation using the MMES technique, including Ag, Au, Al, Co, Cr, Cu, Fe, Ir, Mo, Ni, Pd, Pt, Rh, V, and W. Three hexagonal close-packed metals, Ti, Hf, and Zr, have also shown an improved (001) growth on the (100) Cu.[9]

As suggested before, two determining factors involved in the observed epitaxial growths are the initiation of a heteroepitaxy at the interface, followed by a self-epitaxy, or autoepitaxy, of the metals.[9,10] The results on the growth of a strongly (100)-oriented W film, and a partially (100)-oriented Nb film, both bcc metals, are presented in this paper to illustrate the importance of lattice matching to the interface epitaxy. As for the self-epitaxy, the melting temperatures of the seventeen metals grown epitaxially are compared with the substrate temperature used for an understanding of the fundamental growth of metal films.

The epitaxial growth of W and Nb involves the deposi-

tion of multiple layers in sequence on (100) Si, using an electron-beam evaporation without breaking the vacuum. The (100) Si wafers were degreased, etched in 10 vol.% HF–deionized water, and pull-dried prior to loading into the evaporator. The base pressure of the evaporator is in the low 10^{-7} torr. For W, several structures are compared, W/Cu/Si(100), W/Pd/Cu/Si(100), and W/Au/Pd/Cu/Si(100), Cu being the first layer and W the last layer deposited. For Nb, the following structures are compared: Nb/Cu/Si(100), Nb/Pd/Cu/Si(100), Nb/Au/Pd/Cu/Si(100), and Nb/Mo/Au/Pd/Cu/Si(100). A thickness of 1000 Å was used for each metal layer in these structures, with a deposition rate of about 10 Å/sec. No intentional heating was applied to the substrates during the deposition.

For the growth of W, it is found that neither the Cu nor Pd seed layer allowed an epitaxial growth of (100) W. The W layers deposited show only the (110) orientation, which is the preferred one for the bcc metals. Figure 1 shows the x-ray-diffraction pattern for the W film deposited on the (100) Pd/Cu/Si structure, with similar results using the (100) Cu/Si structure. Only the (110) peak is observed for W, along with the (200) peaks of Pd and Cu. Using Au as the seed layer, with a structure of W/Au/Pd/Cu/Si(100), the W deposited shows a strong (100) orientation, as shown in Fig. 2. A small peak of (110) is still present for the W film deposited. The lattice mismatches involved between W and the seed layers used will be compared later. For the Nb films deposited using Cu, Pd, or Au as the seed layer, only a (110) orientation is observed. An example is shown in Fig. 3 using the Au seed layer. The analysis shows only the (110) peak for Nb, along with the (200) peaks of Au, Pd, and Cu. Using a Mo layer deposited on Au as the seed layer, a (110) peak with much reduced intensity is observed for Nb, along with a (200) one with comparable intensity. This is shown in Fig. 4. The lattice mismatches involved in these structures will also be discussed later.

As discussed elsewhere,[9] the growth of a (100)-oriented bcc lattice on a (100) fcc lattice involves a rotation of 45°

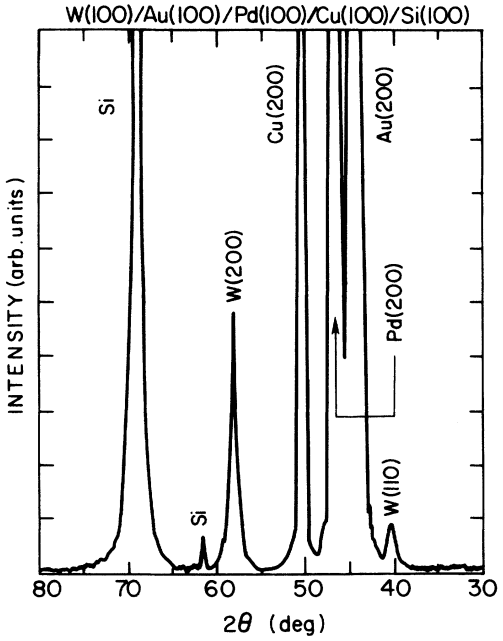

FIG. 2. X-ray-diffraction pattern of the W film deposited on the (100)-oriented Au/Pd/Cu/Si substrate, showing a strong (100) orientation of the W deposited, with a small contribution of the (110) orientation.

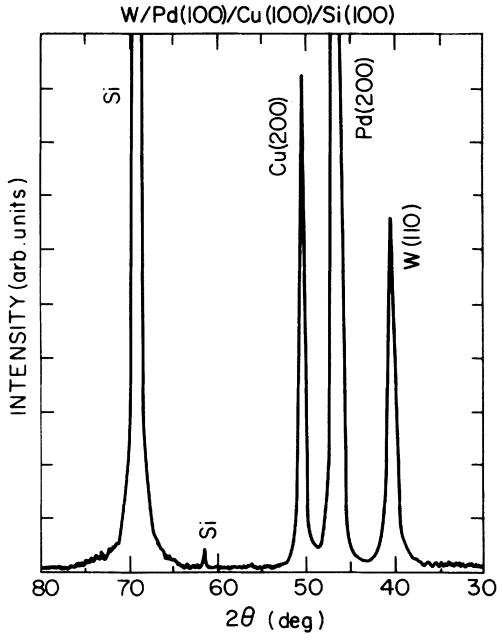

FIG. 1. X-ray-diffraction pattern of the W film deposited on the (100)-oriented Pd/Cu/Si substrate, showing only the (110) orientation of the W deposited.

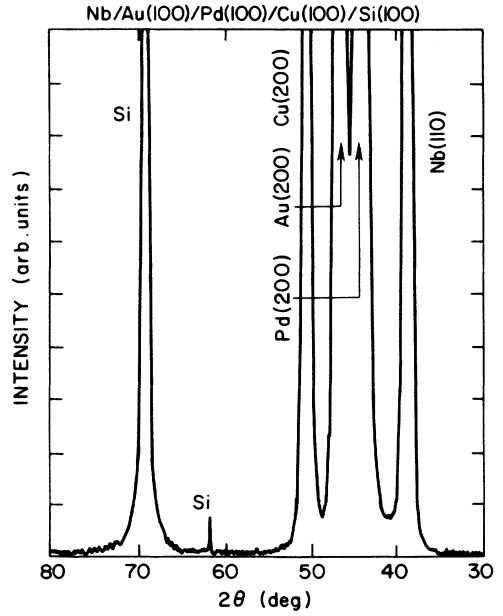

FIG. 3. X-ray-diffraction pattern of the Nb film deposited on the (100)-oriented Au/Pd/Cu/Si substrate, showing only the (110) peak of Nb, and (200) peaks of all the other metals present.

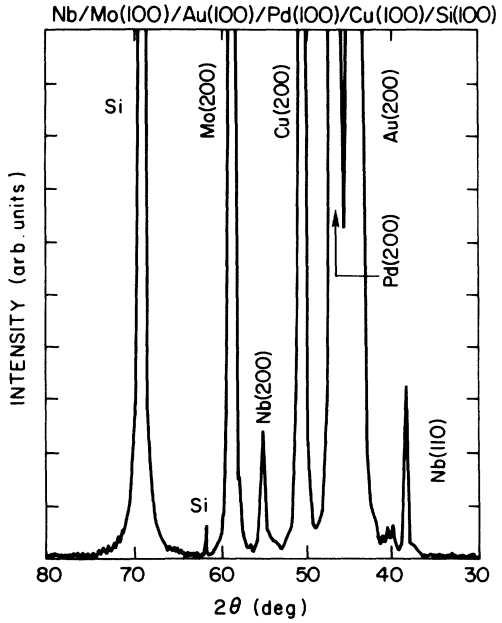

FIG. 4. X-ray-diffraction pattern of the Nb film deposited on the (100) oriented Mo/Au/Pd/Cu/Si substrate, showing both the (110) and (200) peaks of Nb with comparable intensities. All the other metals present show only the (200) diffraction peaks.

of the bcc one around its [001] axis. We have observed such a rotation for the (100) Fe and Cr films deposited on the (100) Pd/Cu/Si substrate.[11] For the (100) plane of a bcc lattice, there is no bonding among the neighboring atoms in the same plane. This makes it very difficult to hold the atoms in such an orientation, unless a favorable bonding exists with the seed layers. Comparing the crystal structures of fcc and bcc lattices, the bonds in the two lattices are off from each other by 45°. A direct growth of a (100) bcc lattice on a (100) fcc one would exert a large distortion in bonding for the bcc layers. A much more favorable bonding would involve a rotation of the bcc lattice by 45°, to minimize the lattice stress due to the misalignment in bonding. With such a rotation, the needed lattice match is altered accordingly. Instead of using the (200) spacings for matching, the (110) spacing of the bcc lattice should be used to match with the (200) one of the fcc lattice. The (200) spacings of W, Au, Pd, and Cu are 1.586, 2.039, 1.945, and 1.808 Å, respectively. Without any rotation of the W lattice relative to those of the Pd and Au ones, the mismatch is 13.1, 20.3, and 25% for the W-Cu, W-Pd, and W-Au interfaces, respectively. With a 45° rotation of the W(100) plane around its [001] axis, a factor of $\sqrt{2}$ is multiplied to its (200) spacing, making it 2.2426 Å. The mismatches with Cu, Pd, and Au become 21.5, 14.2, and 9.5%, respectively. The much-improved lattice match with Au makes the growth of W films favorable with a (100) preferred orientation. It is noted that the mismatch is still large, which is likely the reason for the observation of a small contribution of the (110) orientation of the W films grown on Au. For the cases of Cu and Pd seed layers, the mismatches with W remain too large even after the rotation of the W lattice, consistent with the absence of any (100) growth of W on these metals. Both Nb and Mo are bcc metals, and a (100) growth of Mo has been reported using the Au seed layer.[9] The (200) spacings of Nb and Mo are 1.6519 and 1.574 Å, respectively, with a mismatch of 4.8%. This is compared with a mismatch of 14% for the Nb film deposited on the Au seed layer after the 45° rotation described above. Other examples illustrating the determining role of the lattice matching include the growth of (100) Cr and V, both bcc metals, on Pd but not on Cu.[9] We are currently investigating the in-plane epitaxial relations among all the metals grown sequentially in (100) orientation. Such an epitaxial relation has been observed for the (100) Fe and Cr films, both bcc, and (100) Ni which is a fcc metal.[11] The [110] of Fe and Cr is found to be parallel to the [100] of Cu, while the [100] of Ni is parallel to the [100] of Cu. The determination of such a relation has allowed the study of the angular dependence of the in-plane magnetization of both Fe and Ni using the (100) oriented films.[12] Furthermore, a complete reversal in magnetic anisotropy between the in-plane and out-of-plane magnetizations has been observed for the thin (100)-Ni layer sandwiched between thick (100)-Cu layers.[13]

The observed (100) growth of many metals using the technique described provides an opportunity to look into a fundamental property of the film growth: the minimal

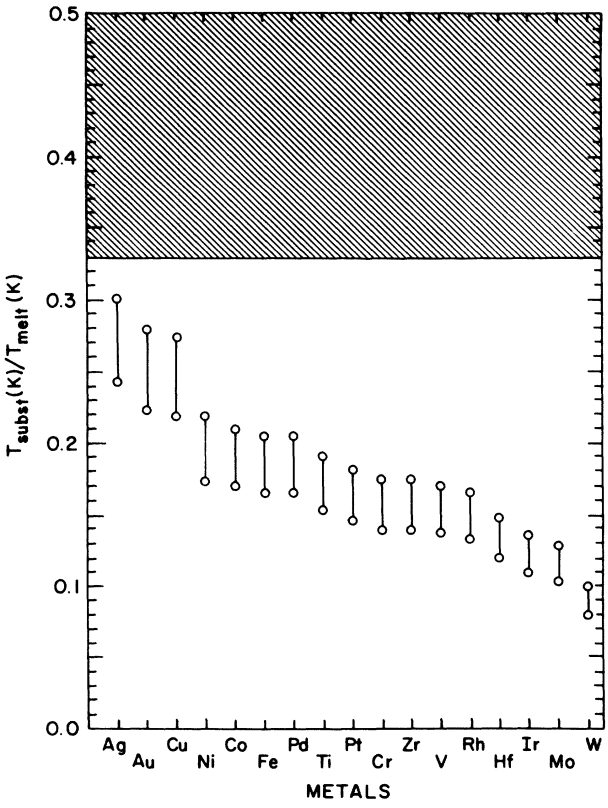

FIG. 5. Plot of substrate-temperature to melting-temperature ratios for seventeen metals that have shown epitaxial growth using the technique of metal-metal epitaxy on silicon. The lower values used 300 K for the substrate temperature, while 473 K is used for the upper values.

temperature needed for the self-epitaxy of the metals. The earlier literature contains reports on some metals using different deposition techniques and conditions,[1-3] making it difficult for a correlation to be established. The MMES technique allows a simple and consistent way to obtain such information for many metals. Our results on W, Nb, and other metals have illustrated that these metals exert a self-epitaxy under the deposition conditions used, provided an interface epitaxy can be initiated.

Thus we have at hand information regarding the minimal substrate temperatures needed for the self-epitaxy of these metals. As mentioned, no intentional heating was applied to the substrate during the deposition process. The substrate surface tempertures can range from room temperatures to higher ones due to the radiation heating from the evaporation source. With water cooling of the sample holder during the evaporation, we have measured a temperature of 39 °C for the holder. In the following discussion, we consider the possibility of even higher surface temperatures, up to 100 °C. We have plotted the ratios of substrate temperatures, T_s, to the melting temperatures, T_m, of the metals, with both T_s and T_m in Kelvin, as shown in Fig. 5. The plots use two substrate temperatures, 300 and 473 K, corresponding to the lower and upper limits shown in Fig. 5, respectively. The shaded area depicts ratios of $\frac{1}{2}$ to $\frac{1}{3}$ mentioned earlier.

It is interesting to notice that all the metals in Fig. 5 have T_s/T_m ratios lower than the $\frac{1}{3}$ value. W is the lowest, with a value of 0.08–0.10 over the substrate temperatures of 300–473 K. An immediate task would be to determine the true minimal ratio of T_s/T_m for each metal. This can be done *in situ* with, for example, low-energy-electron diffraction or reflection high-energy-electron diffraction. By lowering the substrate temperatures in a controlled way, the minimal T_s/T_m ratios needed for the epitaxial growth can be determined for all the metals shown in Fig. 5. The MMES technique allows a simple way of obtaining such ratios for a consistent comparison. The information thus achieved can enchance scientific understanding of metal film growth, and could be applicable to the new ways of making novel structures of metal films.

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[1] *Handbook of Thin Film Technology,* edited by L. I. Maissel and R. Clang (McGraw-Hill, New York, 1970), p. 10-7, and references therein.

[2] *Thin Film Phenomena,* edited by K. L. Chopra (McGraw-Hill, New York, 1969), p. 227.

[3] *Epitaxial Growth,* edited by J. W. Matthews (Academic, New York, 1975), Part A and Part B.

[4] *Molecular Beam Epitaxy and Heterostructures,* edited by L. L. Chang and K. Ploog (Matinus Nijhoff, Hingham, MA, 1985).

[5] *Metallic Superlattices, Artificially Structured Materials,* edited by T. Shinjo and T. Takada (Elsevier, Amsterdam, 1987).

[6] For a comprehensive list of metal epitaxy, see E. Grunbaum, in *Epitaxial Growth* (Ref. 3), Part B, p. 611.

[7] Chin-An Chang, Appl. Phys. Lett. **55**, 2754 (1989); J. Appl. Phys. **67**, 566 (1990).

[8] Chin-An Chang, J. C. Liu, and J. Angillelo, Appl. Phys. Lett. **57**, 2239 (1990).

[9] Chin-An Chang, J. Vac. Technol. A **8**, 3779 (1990); Surf. Sci. (to be published); J. Vac. Technol. A (to be published).

[10] Chin-An Chang, Appl. Phys. Lett. **57**, 297 (1990).

[11] Chin-An Chang and J. Angillelo (unpublished).

[12] Chin-An Chang, J. Magn. Magn. Mater (to be published).

[13] Chin-An Chang, J. Appl. Phys. **68**, 4873 (1990).