RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 32, NUMBER 7 1 OCTOBER 1985

Epitaxial growth and superconducting-transition-temperature anomalies of Mo/V superlattices

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(Received 29 July 1985)

We have epitaxially grown by magnetron sputtering Mo/V superlattices in two different crystalline orientations, (001) and (110), which are determined by our choice of substrate. We have measured T_c as a function of chemical modulation wavelength Λ and find that the behavior cannot be explained by application of proximity-effect theories. We also observe an orientational dependence of T_c which can be understood by effectively rescaling Λ into the number of atomic planes of vanadium in one multilayer period.

The study of metallic superlattices (MSL), while attracting considerable recent interest[1] because of the possibility of creating new material structures with novel properties, is still in its formative stage. Although the number of different MSL's is increasing, the approach to the subject is mainly empirical in the sense that there is as yet no firmly developed body of lore to afford solid predictions as to what will occur when two (or more) metals are grown as a layered structure. The results from a structural point of view have been uneven, with layered materials ranging from the one-dimensional (1D) coherent layers of the sputter-deposited Nb/Cu system[2] to the epitaxially grown single crystals of the electron beam evaporated Nb/Ta system.[3] We report here the preparation, by magnetron sputtering, of epitaxially grown Mo/V superlattices and their superconducting properties. Our results suggest promising paths for future metallic-superlattice research, both in the production of epitaxial films and in the characterization of their superconducting properties. In particular, we report an unexpected behavior of the critical temperature T_c as a function of superlattice wavelength Λ. This behavior cannot be explained by proximity effect alone and suggests that some major change takes place in the superlattice as Λ falls below 70 Å.

The alloy system of Mo and V forms a continuous disordered solid solution in which T_c sharply decreases at a rate of about 0.25 K/at.% as Mo is added to V, and is below 1 K at 20 at.% Mo.[4,5] This behavior cannot be explained by putting normal-state experimental results into the McMillan formula.[5] Vanadium has received considerable attention as a possible spin-fluctuation system,[6,7] so it is not surprising to invoke spin fluctuations as the cause for the discrepancy between theory and experiment in this alloy system.[5] Theoretical calculations[8] also indicate that V will eventually become ferromagnetic if its lattice parameter is stretched enough. Thus we attempted to grow a Mo/V multilayer system in the hope that the relatively large lattice parameter mismatch (about 4.1%) would be accommodated more by interfacial strain than by misfit dislocations, and that this would be reflected in the superconducting behavior as a function of Λ.

We succeeded in growing Mo/V superlattices with two separate crystalline orientations depending on our choice of substrate: the (001) planes of Mo/V parallel to (001) MgO, and the Mo/V (110) planes parallel to $(11\bar{2}0)$ Al_2O_3. We believe this is the first time such structural manipulation of superlattices has been achieved by sputtering. The result is significant because of the large mismatch between the lattice constants of Mo ($a_0 = 3.15$ Å) and V ($a_0 = 3.02$ Å). Previously, only in the e^- beam evaporated Nb/Ta system[3] and our own magnetron sputtered Nb/Ta superlattices[9] on cleaved MgO surfaces has this structural manipulation taken place. Thus it seems that many more metals now become candidates for superlattice systems and various crystalline orientations may be realizable.

The samples were made by magnetron sputtering in an ultrahigh vacuum (UHV) chamber using targets of 99.9% Mo and 99.8% V. The sputtering rates were precalibrated using a quartz-crystal thickness monitor and checked by subjecting certain deposited films to mechanical stylus thickness measurements. The base pressure of the vacuum system was better than 4×10^{-9} Torr, and was held at 10 m Torr during sputtering. Impurity gases were monitored before and after deposition at a flowing argon pressure of 5×10^{-5} Torr using a quadrupole mass spectrometer. At this pressure the total measured impurity content is a factor of 250 less than that of the argon, and the oxygen content was below the sensitivity of the spectrometer, which is 4×10^{-10} Torr. The sputtering rate was 2.5 Å/sec and the substrates were held at a temperature of $\sim 700\,^{\circ}$C during deposition. By adjusting the speed with which the substrates passed beneath the targets, we made a series of samples of equal Mo and V thicknesses with wavelengths from 24 to 250 Å, with total thickness of 2500 Å, on substrates of (001) MgO and $(11\bar{2}0)$ Al_2O_3. Since developing our UHV sputtering system we have successfully grown Nb/Cu multilayers, Nb/Ta superlattices in chosen orientations, and very high quality single-crystal films of Nb and Ta with residual resistance ratios as high as 170.

Figure 1 demonstrates the dramatic effect of temperature on the epitaxial growth of Mo/V on cleaved (001) MgO. The evolving x-ray pattern is that from (001) planes of Mo/V perpendicular to the growth direction. X-ray diffractograms of this type are the characteristic signatures of crystalline multilayers. They reflect the periodic chemical modulation of the multilayer whose wavelength Λ is inversely related to the angular distance between two adjacent peaks.[10] The widths of the peaks also give information about the coherence length in the growth direction, which is about 400 Å for our best samples. The preferred orientation of individual Mo and V deposits is (110). This orientation is observed for all Mo/V superlattices grown on $(11\bar{2}0)$ Al_2O_3, with no detectable presence of (001) Mo/V, just as there is no detectable presence of (110) planes on the dif-

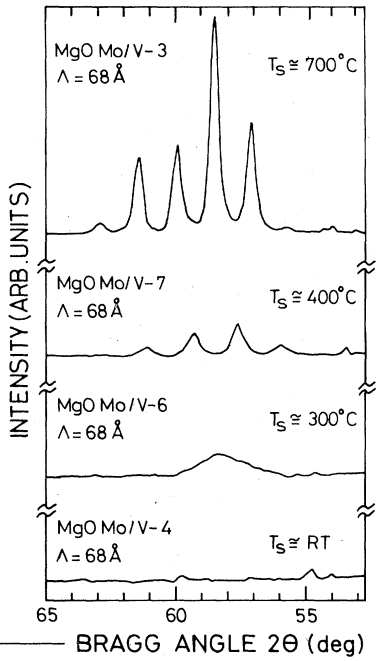

FIG. 1. Intensity vs 2θ diffractograms of different samples on (001) MgO, deposited under the same conditions except for temperature, illustrating growth around 700 °C.

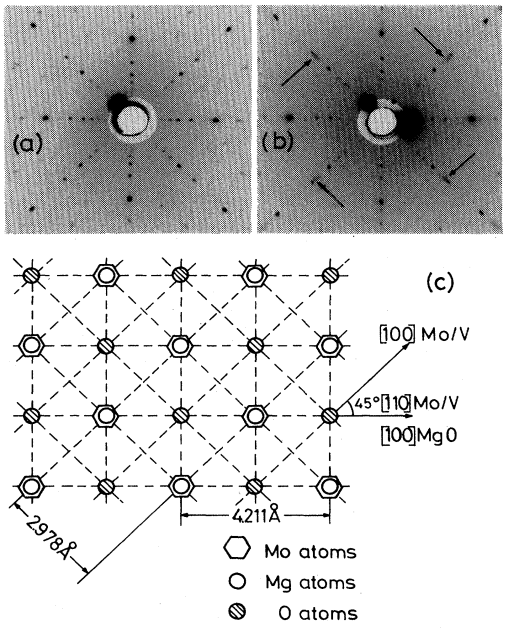

FIG. 2. (a) X-ray back-reflection Laue photographs of MgO, (b) Mo/V on MgO, with four of the typical "additional" points from the Mo/V indicated by arrows, (c) interpretation of (b) as discussed in the text.

fractograms of (001) Mo/V on (001)MgO.

We have developed an x-ray model[11] to help us characterize some structural aspects of the superlattices. The model incorporates lattice strain and interdiffusion and accurately fits the data. The model fits the diffractogram peak positions and the relative intensities of the peaks with a linear strain field and an interdiffusion layer of four lattice planes, thus confirming our initial hope of growth primarily by interfacial strain. The near constancy of the model parameters used to fit all our samples informs us that our evaporation conditions are similar from sample to sample. The model also enables us to determine more precisely what amounts of Mo and V we have deposited since the graphical fit will stray from the experimental data unless precise numbers of atomic planes of each element in one multilayer wavelength are specified. The number of atomic planes is determined from the amount of material deposited per wavelength divided by the value of the interplanar spacing. This number, although somewhat artificial considering the interdiffusion of Mo and V, will be useful when we consider the superconducting properties.

Further x-ray characterization of the Mo/V system is provided by Laue back-reflection photographs. Since it did not prove possible to remove the films from the substrate, we display the Laue photograph of MgO alone and of Mo/V on MgO in Figs. 2(a) and 2(b), respectively. The seemingly additional spots due to Mo/V in Fig. 2(b), only four of which are indicated by arrows, are in fact only rotated 45° from those due to the MgO substrate. This can be interpreted[12] as the (001) plane of Mo/V rotated 45° about the normal to the (001) MgO surface; i.e., (110) Mo/V parallel to (100) MgO [see Fig. 2(c)]. Samples grown on substrates with the temperature lower than ~ 650 °C display Debye-Scherrer rings which are signs of textured growth.

We measured the superconducting-transition temperatures using a four-point ac resistance method. The T_c's of individual 2500-Å films of V on MgO and Al_2O_3, and of Mo on Al_2O_3 were 5.0, 4.8, and 0.62 K, respectively. We present T_c as a function of Λ in Fig. 3(a). Circles represent samples on (001) MgO, squares represent those on $(11\bar{2}0)$ Al_2O_3, solid lines are a guide to the eye, and the dashed line represents a trilayer proximity-effect calculation[13] applied to the (001) samples. The two main features to be noted here are the sharp drop in T_c beginning at about $\Lambda = 70$ and 60 Å for (110) and (001) samples, respectively, and the orientational dependence of T_c.

The first reaction to the sharp drop in T_c is simply that, because of interdiffusion, there is an alloylike interfacial layer whose low T_c becomes more dominant as Λ decreases. Thus we attempted to fit the data using a trilayer proximity-effect calculation similar to that used by Lowe and Geballe[13] to analyze T_c behavior of Nb/Zr multilayers. Briefly, the proximity-effect theory[14] of Cooper and de Gennes for thin bilayers is that when the thickness of the bilayers is much less than the coherence length, the Cooper pairs experience an effective attractive interaction $[N(0)V]_{\text{eff}}$ which is the spatial average of the potentials from both metals. This effective interaction is used in the BCS expression

$$T_{cs} = 1.14\Theta_D \exp\{-1/[N(0)V]_{\text{eff}}\} \quad . \tag{1}$$

Lowe and Geballe have included the effect of an interfacial alloy layer on T_c and have written the effective interaction as

$$[N(0)V]_{\text{eff}} = \frac{N_A^2 V_A d_A + N_B^2 V_B d_B + N_I^2 V_I d_I}{N_A d_A + N_B d_B + N_I d_I} \quad , \tag{2}$$

where d_A, d_B, and d_I are the thicknesses of the metal A

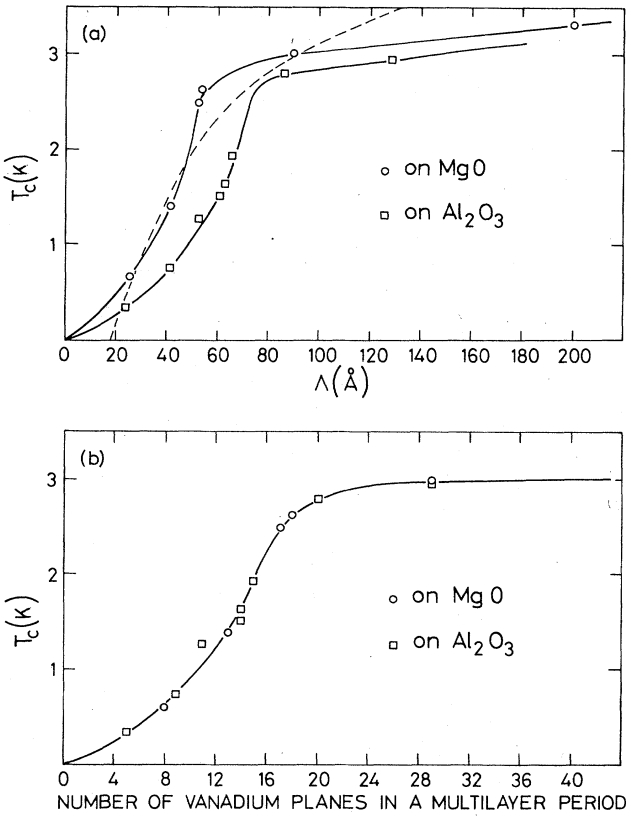

FIG. 3. (a) T_c as a function of Λ for both (001) and (110) Mo/V samples. The dashed line is a proximity-effect calculation as discussed in the text. (b) T_c replotted as a function of the number of vanadium planes for both orientations. The solid lines in (a) and (b) are a guide to the eye.

layers, metal B layers, and twice the interfacial layers, respectively, and $\Lambda = d_A + d_B + d_I$. By setting $d_I = 0$, $[N(0)V]_{\text{eff}}$ reverts to the usual form.[14] We extended the above analysis by assuming a composition gradient, determined in part by the x-ray fit, over the interfacial layer, used published data[4,5] on the alloy series, and integrated the interfacial terms in Eq. (2) over the interfacial thickness. To arrive at the dashed curve in Fig. 3(a) we have assumed similar diffusion profiles for all samples with an interfacial layer thickness of 8 Å, which is consistent with the x-ray fit. This is a reasonable assumption because the multilayers were deposited with approximately the same substrate temperatures and for the same times. The x-ray model fits reinforce this assumption. As can be seen, this trilayer calculation, while showing a significant drop in T_c at short Λ, cannot explain the character of the data. Only by allowing the diffusion profiles to range by 50% about a mean can one fit the data. Since this is highly unlikely, we assume there is an additional mechanism suppressing superconductivity in these materials. We have also attempted to apply the Werthamer theory of bilayers[15] to this system by first applying it to the "bilayer" of Mo and interface, and then combining this with the vanadium layer. The results were not appreciably different than the trilayer calculation just described. The main point is that any proximity calculation is bound to give a smooth variation of T_c and cannot reproduce the sudden drop of T_c around $\Lambda = 70$ Å. One of the results of the x-ray fit is that the lattice is distorted: The interfacial layer is not really an alloy with isotropic lattice constants but one where the lattice is stretched perpendicular, and compressed parallel, to the growth direction. This may, for instance, enhance the magnetic susceptibility of the system and thus affect T_c via spin fluctuations.

Referring now to Fig. 3(b), we have eliminated the surprising orientational dependence by replotting T_c as a function of the number of vanadium layers. As mentioned before, this parameter by itself ignores interdiffusion but it does take into account the difference of the interplanar spacing between the (001) planes and the (110) planes. For a given amount of material deposited there will be a factor of $\sqrt{2}$ times more (001) planes grown parallel to MgO than (110) planes grown on Al_2O_3. Since alloying by diffusion is probably the dominant mechanism suppressing T_c in the low Λ region, in order to explain Fig. 3(b) we must make the unusual assumption that the probability for an atom to diffuse to an adjacent atomic plane is equal for both the (001) and (110) planar spacings, even though this distance differs by a factor of $\sqrt{2}$. Thus samples with equal numbers of V planes (but not equal wavelengths) will have the same number of interfacial planes, and hence similar T_c's.

The low-wavelength character of the superconducting-transition temperature, as well as its epitaxially induced orientational dependence, are new and exciting features of this Mo/V superlattice system that, while requiring further investigation, are indicative of some of the novel properties that can be achieved by the multiple layering of different metals.

We wish to thank Dr. J. Geerk and Dr. E. Walker for invaluable technical advice and assistance. We thank Y. Jeanrenaud and E. Perreard for building some of the sputtering equipment.

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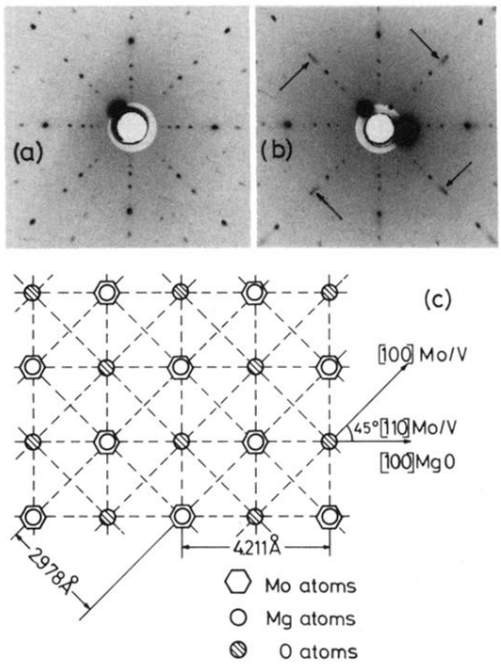

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