Electronic structure of amorphous Mo-Ru-Si alloys

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The results of x-ray photoemission spectroscopy (XPS) and electrical resistivity measurements on amorphous metal alloys of the form $(Mo_{1-x}Ru_x)_{80}Si_{20}$ are reported. The XPS valence band spectra are dominated by the Mo-4*d* subbands and the electronic structure of the amorphous alloys can best be described in the virtual crystal limit of the coherent potential approximation (CPA) formalism. The density of electronic states at the Fermi level sharply decreases in the alloys as the Ru/Mo ratio is increased. Associated with this drop is an increase in electrical resistivity and decrease in the superconducting transition temperatures of the alloys. These relationships are discussed in the context of current theories of the electrical resistivity and superconductivity in amorphous alloys.

EXPERIMENTAL PROCEDURE AND RESULTS

Amorphous metal thin films of composition $(Mo_{1-x}Ru_x)_{80}Si_{20}$ ($x = 0.00$, 0.27, 0.76, and 0.92) were prepared by magnetron sputtering in an Ar atmosphere using a Research *S*-Gun.[1] The samples, approximately 1 μm thick, were prepared on titanium or glass substrates at room temperature. The XPS measurements on the films were performed using a Kratos XSAM 800 spectrometer. A Mg K_α (1253.6 eV) anode was used as the excitation source operated at 300 W. The instrument resolution was 1.1 eV for valence band data. The surface of each of the samples was sputtered using an argon-ion beam (25 $\mu A/cm^2$) to remove any metal oxides that had formed. Electrical resistivity measurements were made on the samples deposited on glass using a four-point contact probe at room temperature. The thickness of the films was determined by a Dektak-2 profilometer.

The x-ray diffraction measurements confirmed that all the samples of this study were amorphous. Amorphous phase formation in the ternary Mo-Ru-Si system has been previously reported by Johnson and Williams[2] and Poon.[3] The results of the XPS measurements are shown in Fig. 1 for the Mo-Ru-Si alloys. The results of the electrical resistivity measurements are displayed in Fig. 2 as a function of the Ru content of the amorphous alloys. A nearly linear increase in the resistivity is observed as the Ru content of the alloys is increased.

DISCUSSION

The electronic structure of Mo-Ru-Si amorphous alloys

The valence band of the Mo-Ru-Si alloys consists of a single broad feature. This broad feature is expected to arise from the Mo-4*d* and Ru-4*d* electronic states. The photoemission cross sections for Mo-5*s*, Ru-5*s*, Si-3*p*, and Si-3*s* states are on the order of a hundred times smaller than that of the 4*d* Mo and Ru states. Using a renormalized atom technique, Hodges *et al.*[4] have calculated the average *d*-band energy and width for the 3*d* and 4*d* transition metals. From their calculations, the difference in energy of the centroids of the Mo-4*d* and Ru-4*d* subbands is 1.6 eV and the width of the subbands is about 10.5 eV. Thus, the two primary contributions to the valence band of the alloys of this work strongly overlap and result in a single broad feature. Within the context of a coherent potential approximation (CPA) calculation,[5] the alloys of this study should be described as being in the virtual crystal limit. The condition for considering an alloy to be in the virtual crystal limit is to have the quantity (δ)

$$\delta = (\epsilon^A - \epsilon^B)/w \tag{1}$$

to be much less than 1, where ϵ^A and ϵ^B are the centroids of the *d* bands and w is one-half the bandwidth. In the case of Mo-Ru-Si alloys, using the renormalized values of Hodges *et al.*[4] for the energy levels and bandwidth, $\delta = 0.15$. In the CPA calculations, the virtual crystal limit corresponds in

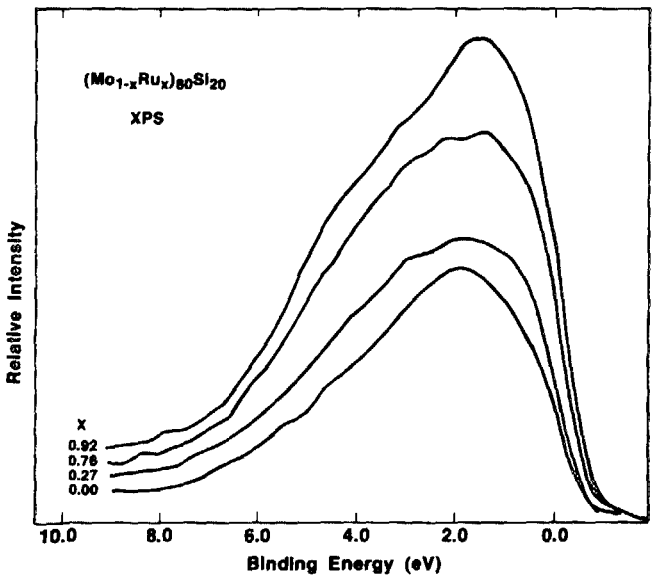

FIG. 1. Valence band spectra of amorphous Mo-Ru-Si alloys. The zero of the binding energy corresponds to the Fermi edge.

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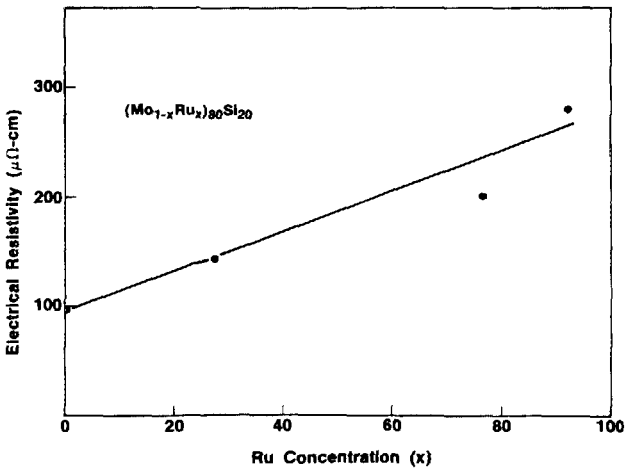

FIG. 2. Results of electrical resistivity measurements in amorphous Mo-Ru-Si alloys as a function of Ru concentration.

first order in to the familiar rigid-band approximation. Corrections to this description are on the order of δ^2. The virtual crystal limit or rigid band approximation would predict an undistorted shift of the common d band upon alloying. This is consistent with the data of Fig. 1 in which a filling of the d band occurs without apparent changes in the d-band shape as the amount of Ru in the alloy increases.

Of special interest in the present work is the d band density of electronic states at the Fermi energy $[D_d(0)]$ as a function of Ru content in the alloys. This determination is difficult due to the poor resolution of the XPS data. Two approaches were used to extract $D_d(0)$ from the XPS data. The first is to simply relate the area (corrected by the relative cross section for photoemission for Mo-4d and Ru-4d states[6]) under the XPS curves to the occupation of the common 4d band. $D_d(0)$ can be obtained by assuming a smoothly varying d-band shape (such as that of the Hubbard model[7]). The second approach uses a CPA calculation in the virtual crystal approximation to simulate the XPS spectra. These simulated spectra are then compared to the experimentally observed data. Both of these methods give essentially the same results for $D_d(0)$ as a function of Ru content. The values are listed in Table I having been normalized to the value of 1.0 states/eV atom for each spin state for amorphous $Mo_{80}Si_{20}$. This value was chosen to bring the $D_d(0)$ values into agreement with previous heat capacity and magnetic susceptibility data on Mo-based amorphous alloys.[8] The $D_d(0)$ values in Table I monotonically decrease as the Ru content of the alloys is increased. Starting from $Mo_{80}Si_{20}$ in which $D_d(0)$ falls near the maximum of the 4d band, the addition of Ru results in a filling of this band and hence in a lowering of $D_d(0)$.

TABLE I. d-band density of states at the Fermi level for amorphous $(Mo_{1-x}Ru_x)_{80}Si_{20}$ alloys. The values have been normalized to a value of 1.00 states/eV atom for each spin state for amorphous $Mo_{80}Si_{20}$.

Composition (x)	d-band density of states (states/eV atom spin)
0.00	1.00
0.27	0.78
0.76	0.57
0.92	0.35

Electrical resistivity of Mo-Ru-Si amorphous alloys

A variety of theories have been proposed for the electrical resistivity of amorphous metals. A recent review of this subject has been given by Naugle[9] and will be used in this discussion. Of the four theoretical models Naugle identified, the most commonly applied models are the Ziman–Faber diffraction model and the Mott s-d scattering model. For transition metals, the Ziman–Faber diffraction model has been extended by Evans *et al.*[10] to obtain the result

$$\rho \approx \frac{30\pi^3 h^3}{me^2\Omega_0 K_F^2 \epsilon_F} \sin^2 \eta_2(\epsilon_F) a(2K_F), \tag{2}$$

where the symbols have their usual meaning[9] and where $a(2K_F)$ includes the partial structure factors of the alloy. A direct comparison of our resistivity values with Eq. (2) is difficult due to the uncertainties in quantities such as $a(2K_f)$ and K_F. However, since the width of the d resonance and the structure factor are roughly constant here as the alloy composition is varied, the effect of replacing Mo by Ru would be to increase the energy difference between the d resonance and E_F and thereby lower the electrical resistivity. The Mott s-d scattering model would also predict a decrease in resistivity as the Ru content is increased. In this case, Brown *et al.*[11] obtained the result

$$\rho \approx \frac{12\pi^4 h K_F \Gamma}{e^2 K_0^5} N_d(\epsilon_F), \tag{3}$$

where Γ is the width of the d resonance and $N_d(E_F)$ is the density of d states at the Fermi level [designated in the present work as $D_d(0)$]. With Γ constant as in the present alloy, the resistivity in the Mott s-d scattering model would be expected to increase as $D_d(0)$ is increased.

Some recent work has emphasized the strong scattering aspects of the electronic conduction process in amorphous and liquid metals.[12–14] From Ballantine *et al.*[14] and Schultz

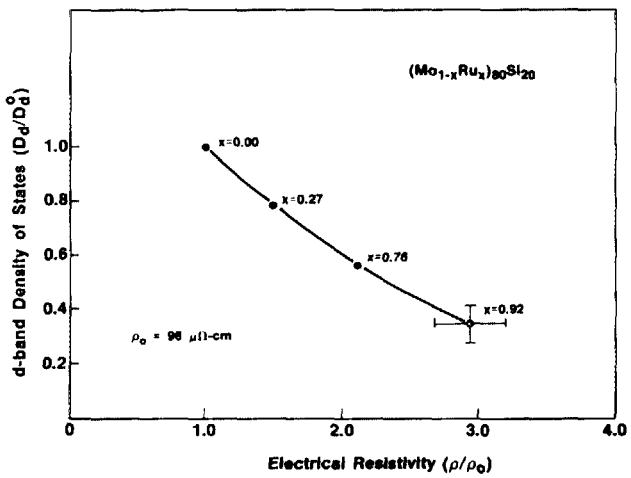

FIG. 3. Correlation between the d-band density of states at the Fermi edge (normalized by $D_d^0 = 1.0$ states/eV atom for each spin state) and the electrical resistivity (normalized by the value for amorphous $Mo_{80}Si_{20}$–96 $\mu\Omega$ cm).

TABLE II. Superconducting transition temperatures for some amorphous $(Mo_{1-x}Ru_x)_{80}Si_{20}$ alloys from Ref. 3.

Compositions (x)	Sueprconducting transition temperature (K)
0.40	5.80
0.70	4.66
0.80	3.14
0.90	2.31

and Johnson,[15] one interesting insight that has emerged is the possible important role of d electrons in the electrical conductivity of liquid and amorphous transition metals. This insight stems from the result that for some liquid transition metals such as La, the electronic diffusivities of s and d electrons are comparable. One can write the separate contributions to the electrical conductivity as

$$\sigma = \sigma_s + \sigma_d. \tag{4}$$

In amorphous metal alloys where the d electrons constitute a majority of the states at the Fermi level, the d electrons may determine the elecrical conductivity. Figure 3 shows the experimentally determined correlation between the d band density of states at E_F from the XPS measurements and the electrical resistivity. This correlation may indicate that in these alloys d band conduction is occurring and in fact determining the compositional behavior of the resistivity.

Superconductivity in Mo-Ru-Si amorphous alloys

A considerable amount of work has been reported on the superconducting properties of Mo-based amorphous alloys (see Refs. 8, 16, and 17, for example). Poon and Carter[3] have measured the superconducting transition temperatures for a wide variety of Mo-Ru amorphous films. Their values for alloys similar to those of the present work are listed in Table II. In their work, Poon and Carter stressed the relationship between T_C and the electronic density of states in alloys of this type and showed that the decrease in T_C as Ru is added to the alloys of Table II can be understood in terms of a reduction of $D_d(0)$. The present XPS results provide direct evidence for their explanation, since upon comparing Table I and II a direct relationship between T_C and $D_d(0)$ is observed.

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