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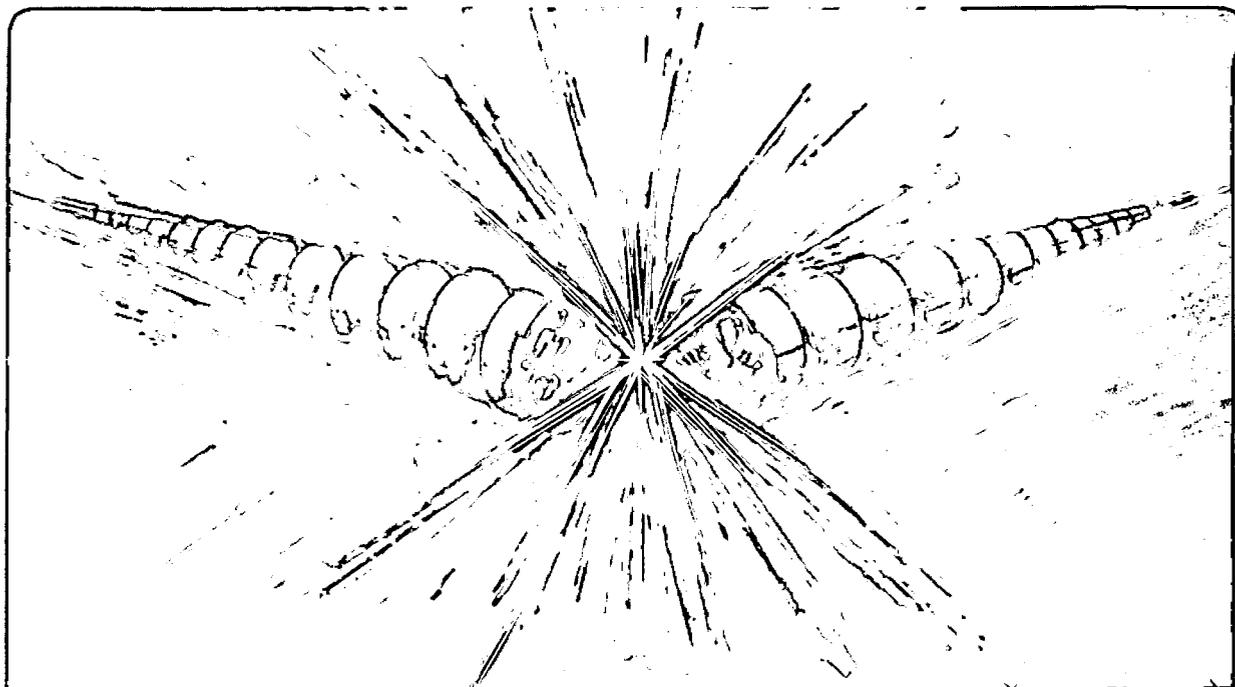
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**THE MICROSTRUCTURAL EVOLUTION OF
NANOMETER RUTHENIUM FILMS IN Ru/C MULTILAYERS
WITH THERMAL TREATMENTS**

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THE MICROSTRUCTURAL EVOLUTION OF NANOMETER RUTHENIUM FILMS IN Ru/C MULTILAYERS WITH THERMAL TREATMENTS

ABSTRACT

The evolution of nanometer Ru films sandwiched between various C layer thicknesses with thermal treatments was studied by plan-view and cross-sectional Transmission Electron Microscopy. Plan-view observation provides information on the Ru grain size, while cross-sectional studies allow examination of the multilayer morphology. After annealing at 800°C for 30 minutes, the grain size in the 2 and 4 nm Ru layers show little difference from each other, while that in the 1 nm Ru layers depends strongly on the thickness of the C layers in the multilayers. It increases with decreasing C layer thickness. Agglomeration of the Ru layers is observed in 1nm Ru / 1nm C multilayers after annealing at 600°C for 30 minutes. The evolution of the microstructures and layered structure stability of the Ru/C system is compared to that of W/C and Ru/B₄C systems.

INTRODUCTION

Multilayer structures containing alternating layers of high and low atomic number materials provide highest reflectivity in the region of the electromagnetic spectrum from extreme ultra-violet to x-ray wavelengths.¹ Multilayers having carbon as the low Z material yield practical reflectivities at normal incidence at wavelengths between 4.5 and 12.5 nm. As

the operating wavelength decreases, the period or layer thicknesses inside the multilayers also decreases, and imperfections in the layered microstructure have increasing effects on the multilayer reflectance and stability. As-deposited nanometer-period multilayers are in a metastable configuration. The microstructures depend on, among other factors, the evolution of the metal layers with thermal treatments and its reactions with the specific materials which make up the multilayers. Annealing studies therefore are useful in understanding the microstructural evolution of the multilayers toward equilibrium, the relative stability of multilayers composed of different materials, and to simulate long-term or elevated temperature applications of x-ray multilayers.

The microstructural characteristics of the layers of a metal/carbon multilayer depend on the reactions between the metal and carbon constituents which can be predicted from the appropriate phase diagram. The Ru/C system was studied because of its potential high performance compared to other metal/carbon systems at the soft x-ray wavelengths. The Ru-C phase diagram is of simple eutectic type, with Ru and C having very low mutual solubilities at low temperature. Previous studies show that the amorphous Ru layers in a 2 nm period multilayer agglomerate, while thicker crystalline layers in longer period multilayers do not, under the same annealing conditions.² The thin amorphous Ru layers are in a high energy non-equilibrium state, which provides a strong driving force for crystallization through diffusive rearrangements of the atoms. Annealing of W/C multilayers of different periods, however, does not result in agglomeration of the metal layers.³ The W layers in the 2 nm period W/C multilayers remain amorphous, while formation of a carbide phase was instead found in longer periods, in contrast to the formation of elemental Ru crystallites in the Ru/C system. In this paper, we investigate the effects of thermal treatments upon the microstructural evolution of Ru films sandwiched between C layers, and of agglomeration of the thin Ru films after annealing. Existing models for thin film agglomeration, and their relevance to these nanometer thick films are discussed. The phases present in, and the layered structure stability of, the Ru layers in

Ru/C multilayers are compared to those of the W layers in W/C multilayers, and of the Ru layers in Ru/B₄C multilayers.

EXPERIMENTAL TECHNIQUES

Samples were prepared by magnetron sputtering at floating temperature at the Center for X-Ray Optics, LBL. The apparatus and procedures of deposition have been described elsewhere.⁴ Samples of nominally 1, 2, and 4 nm Ru layer thicknesses were prepared as multilayers sandwiched between various thicknesses of C films. Three thicknesses of C were deposited for each Ru thickness, such that the Ru-to-C layer thickness ratios were 0.5, 1, and 2. The nanometer thicknesses of the Ru and C layers in the Ru/C multilayer samples containing the 1 nm thick Ru layers hence were 1/2, 1/1, and 1/0.5. Similarly, the layer thicknesses of the samples containing the 2 and 4 nm thick Ru layers were 2/4, 2/2, 2/1, and 4/8, 4/4, and 4/2, respectively. Different periods of W/C and Ru/B₄C multilayers, with the high Z material layer composed of approximately 40% of the multilayer periods, were also prepared for the studies. A B₄C alloy target was used in sputtering of the B₄C films.

Cross-sectional and plan-view Transmission Electron Microscopy (TEM) were used to characterize the films. Cross-sectional samples from multilayers deposited on standard Si (111) wafers were prepared by mechanical thinning, followed by ion beam milling in a cold stage.⁵ Plan-view samples were prepared so that the multilayers spanned the holes of the TEM copper grids.⁶ Annealing of the samples was performed in a vacuum furnace at 10⁻⁶ torr. The cross-sectional samples were studied in a JEOL JEM 200CX electron microscope equipped with high resolution goniometer, operating at 200 kV. The plan-view samples were studied in a Philips 301 operating at 100 kV.

RESULTS AND DISCUSSION

Plan-view TEM observation

Plan-view TEM observation of the as-prepared samples reveals that the structures are predominantly amorphous for the 1 and 2 nm Ru films, and show signs of micro-crystallites in the 4 nm Ru films, for all thicknesses of C films prepared. The plan-view TEM samples annealed at 400°C for 2 minutes and for 30 minutes show no significant differences in the microstructure from the as-prepared samples. The electron diffraction patterns from all three Ru film thicknesses show very diffuse rings signifying a predominantly amorphous structure. Further annealing at 600°C for 30 minutes results in elemental Ru micro-crystallites with grain size of the order of a few nanometers. Annealing at higher temperature or longer time was required to induce further grain growth or coarsening of these grains.

The plan-view TEM images in Figure 1 exhibit the microstructures of Ru crystallites for the three thicknesses of Ru films sandwiched between different thicknesses of C films after annealing at 800°C for 30 minutes. The bright field images in Figures 1a)-i) display the images of samples with the same Ru layer thickness in each row; 1 nm, 2 nm, and 4 nm thick Ru layers are in the first, second, and third row, respectively. Each column in Figure 1 has the same Ru-to-C layer thickness ratio of 0.5, 1, and 2, in the right, center, and left column, respectively. The electron diffraction patterns of the 4 nm Ru layer thickness samples in Figures 1g)-i) are shown as example in Figures 1k)-m). The polycrystalline rings in these diffraction patterns originate from elemental Ru crystallites.

Several trends in Ru grain size are apparent from Figure 1. First, the grain size distribution in samples with 2 and 4 nm thick Ru layers in Figures 1d)-i) shows little difference from each other. The Ru grain size in these samples is of the same order as the Ru film thickness, consistent with the grain size observed from cross-sectional TEM

samples. Second, and in contrast to the 2 and 4 Ru layers, the grain size in the 1 nm Ru film increases with decreasing C film thickness. These thinnest as-deposited Ru layers studied are the most highly disordered and hence have the strongest driving force for crystallization. Higher surface-to-volume ratios of structures with thinner C layers may also enhance the kinetics of crystallization and grain growth of the Ru crystallites. Evidently, the thinner C layers increase the mobility of the Ru atoms in the annealing-induced crystallization and grain growth, which results in larger final grain distribution. Indeed it is possible that the thinnest C layers in Figure 1c) may not be continuous in the as-deposited sample. The microstructure of the 1nm Ru / 2nm C multilayer in Figure 1a) shows a highly dispersed composite of approximately one-nanometer diameter grains of Ru in a C matrix. Third, comparison of Figures 1c), f), and i) of the samples with the same Ru-to-C layer thickness ratio also indicates that the grain size increases with decreasing layer thickness of Ru and/or C. Thus thinner as-deposited Ru layers result in larger Ru grain sizes, contrary to the expectation that grain size is proportional to the film thickness. Evidently, the larger annealed grain size in the thinner layers results either from increased kinetics of crystallization and grain growth with thinner C layers, or from the higher degree of metastability in the thinner Ru layers.

Cross-sectional TEM samples

Our previous study indicates that the thicker Ru layers are stable while the thinner layers agglomerate upon annealing.² In this study, samples of 1nm Ru / 1nm C treated under various annealing conditions were examined in cross-section to study the microstructures and morphology of the films. Figure 2 demonstrates the evolution of microstructure of this multilayer with different thermal treatments. Shown in each frame of Figure 2a)-d) are the cross-sectional HRTEM image of ten bilayers of Ru and C films deposited on a thick C buffer layer prepared on a Si substrate (not shown), and its

corresponding electron diffraction pattern. The amorphous layer on top of the multilayers is the epoxy adhesive used in the cross-sectional TEM specimen preparation process. The small-lattice-spacing diffraction spots in the diffraction patterns of Figures 2a)-c) arise from the epitaxial Si substrate.

The layered structure of the as-prepared sample is shown in Figure 2a). Both the bright field image and the diffraction pattern indicate that the structure is predominantly amorphous. After a thermal treatment of 400°C for 2 minutes in vacuum, the layered structure is still stable and displays an amorphous structure within the layers, as seen in Figure 2b). Annealing at 600°C for 30 minutes, however, results in destruction of the layered structure by agglomeration of the Ru films, shown in Figure 2c). The Ru films have agglomerated and crystallized into almost spherical crystallites with diameters on the order of a few nanometers, similar to that observed in the plan-view samples. The sizes of these crystallites are much larger than the initial bilayer thickness of the multilayer, which suggests that during agglomeration, Ru from adjacent layers may coalesce. The rings in the diffraction pattern indicate a preferred orientation with the $\langle 101 \rangle$ direction of the elemental Ru normal to the film surface, similar to results reported earlier.²

The interface between the agglomerated multilayer and the C buffer layer appears quite uniform and continuous in Figure 2c). After the sample was ion-milled to a thickness transparent to the electron beam, the multilayer has a trapezoid configuration in the wedged-shape TEM specimen where the multilayer / carbon interface is the base of the trapezoid. Imaging with the electron beam parallel to the base of the trapezoid thus produces an image from a thick region of many Ru grains, and results in an image of a smooth and uniform interface. A single layer of Ru grains at one corner of the base of the trapezoid sample can be viewed by tilting the TEM specimen in the direction perpendicular to the film surface. The interface then appears like that of an agglomerated structure, as seen in Figure 2d). The morphology of single Ru grains is seen to be almost spherical crystallites that do not appear to be connected to each other. Similar morphologies occur at the surface of the

agglomerated structure, which is the interface between the multilayer and the epoxy layer in this Figure.

Existing models for agglomeration

Mechanisms for agglomeration of thin films have been studied by various groups,⁷⁻¹⁰ although they were developed for films that are substantially thicker than those in this study. One model is analogous to the Rayleigh instability in an infinitely long cylinder with isotropic surface energy, in which perturbation of the straight cylinder walls drives the structure to a spherical shape in order to reduce the surface area. When applied to thin films, linear stability analysis predicts that all small perturbations decay and a flat film should remain stable.⁷ Studies of systems with large perturbations (amplitudes of the same order as the film thickness) require nonlinear stability analysis.⁸ Energy calculations show that a film can actually be ruptured if the amplitudes of the perturbations are large enough, and that perturbations with amplitudes smaller than the film thickness will decay.

Another model of agglomeration is based upon the mechanism of grain boundary grooving in polycrystalline thin films,⁸⁻¹⁰ which predicts that agglomeration in polycrystalline films results from the deepening of the grooves at grain junctions, driven by the equilibrium interfacial energies during grain growth. In general, agglomeration in polycrystalline films from grain boundary grooving is observed when the crystalline grain size to film thickness ratio reaches a critical value that is greater than 1.

The existing models are not necessarily appropriate to explain for the agglomeration mechanisms of the one-nanometer metal films in this study. The initial Ru films are effectively only 3 to 4 atomic layers thick and are amorphous before agglomeration. The multilayer structure here is far from the equilibrium state. The high free energy of the amorphous Ru layers relative to crystalline Ru provides an additional driving force for crystallization and/or agglomeration which is not considered in these models. In addition, it

is difficult to differentiate the bulk from the interfacial properties at this thickness. Simple calculation of the surface areas, assuming uniform microstructure and equal interfacial energies for amorphous and crystalline structures, indicates that agglomeration occurs more readily in thinner films, and that a spherical morphology is preferred to a flat film when the grain size is larger than the film thickness. This is consistent with the values in the reported models,⁸⁻¹⁰ and with the measured values from the agglomerated structure in Figure 2. It is not clear whether crystallization or agglomeration occurs first for these 1 nm thick layers since they are so thin. Grain boundary grooving of the polycrystalline layered films that have crystallized from the initial amorphous state is possible; the equilibrium dihedral angles at the grain junctions however cannot be observed in the images since the crystalline Ru grains appear to be separated by a thick C grain boundary region.

Comparison with compound forming systems

The evolution of the Ru layers in Ru/C multilayers with annealing is different from that of the W layers in W/C multilayers and that of the Ru layers in Ru/B₄C multilayers. Previous studies found that annealing of W/C multilayers of 2 nm period at 500°C for 4 hours does not result in agglomeration of the W layers.³ Diffusion of the C atoms into the W films forms a phase that stabilizes in an amorphous state and lowers the energy of the system, and hence the structure remains layered. A carbide (W₂C) is formed in thicker period W/C multilayers after annealing under the same conditions.²

Preliminary studies of the microstructure and layered structure stability in Ru films between boron carbide layers reveal similar evolution to that of the W/C system. Examination of 1.1 nm Ru films between 1.7 nm B₄C layers indicates that the films remain layered and continuous upon annealing at 600°C for 30 minutes. Both the as-prepared and annealed Ru/B₄C multilayers show predominantly amorphous structure at this period. Longer period Ru/B₄C multilayers also remain layered after annealing, and crystallization or

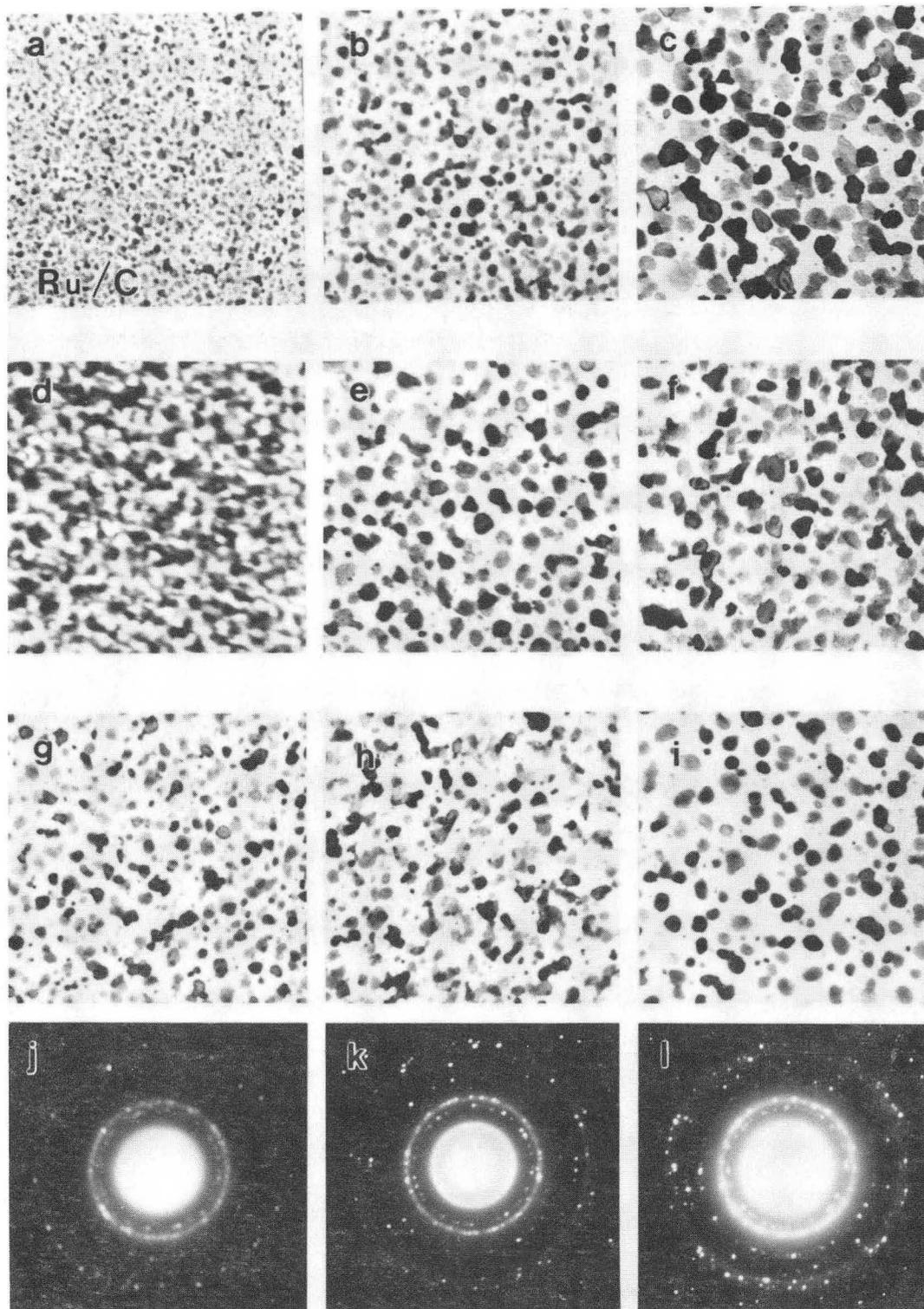
recrystallization of the Ru layers to form a boride phase (RuB_2) is observed from the electron diffraction patterns of plan-view samples. Compound formation in this system, similar to that of W/C, may have stabilized the layered structure of the thin metal films upon annealing. Agglomeration of the Ru films in the Ru/C system, in contrast to the stable layered structure in the W/C and the Ru/B₄C systems, appears to be related to the immiscible region in its phase diagram, which promotes phase separation between the Ru and the C constituents.

CONCLUSIONS

The microstructural evolution of thin Ru layers sandwiched between C layers was studied using cross-sectional and plan-view TEM. The Ru grain size distribution in the annealed multilayers is a function of the thicknesses of both the metal and the carbon layers, as observed in plan-view samples. The grain size dependence is more apparent in the thinner Ru and C layers, in which high surface-to-volume ratio provides a stronger driving force for crystallization and grain growth of the Ru. Agglomeration of the 1 nm Ru layers between 1 nm C layers is observed after annealing at 600°C for 30 minutes by cross-sectional TEM. Annealing of W layers between C layers and of Ru layers between B₄C layers of comparable thicknesses does not result in agglomeration in the thinner films, and leads to formation of a crystalline compound in the thicker films.

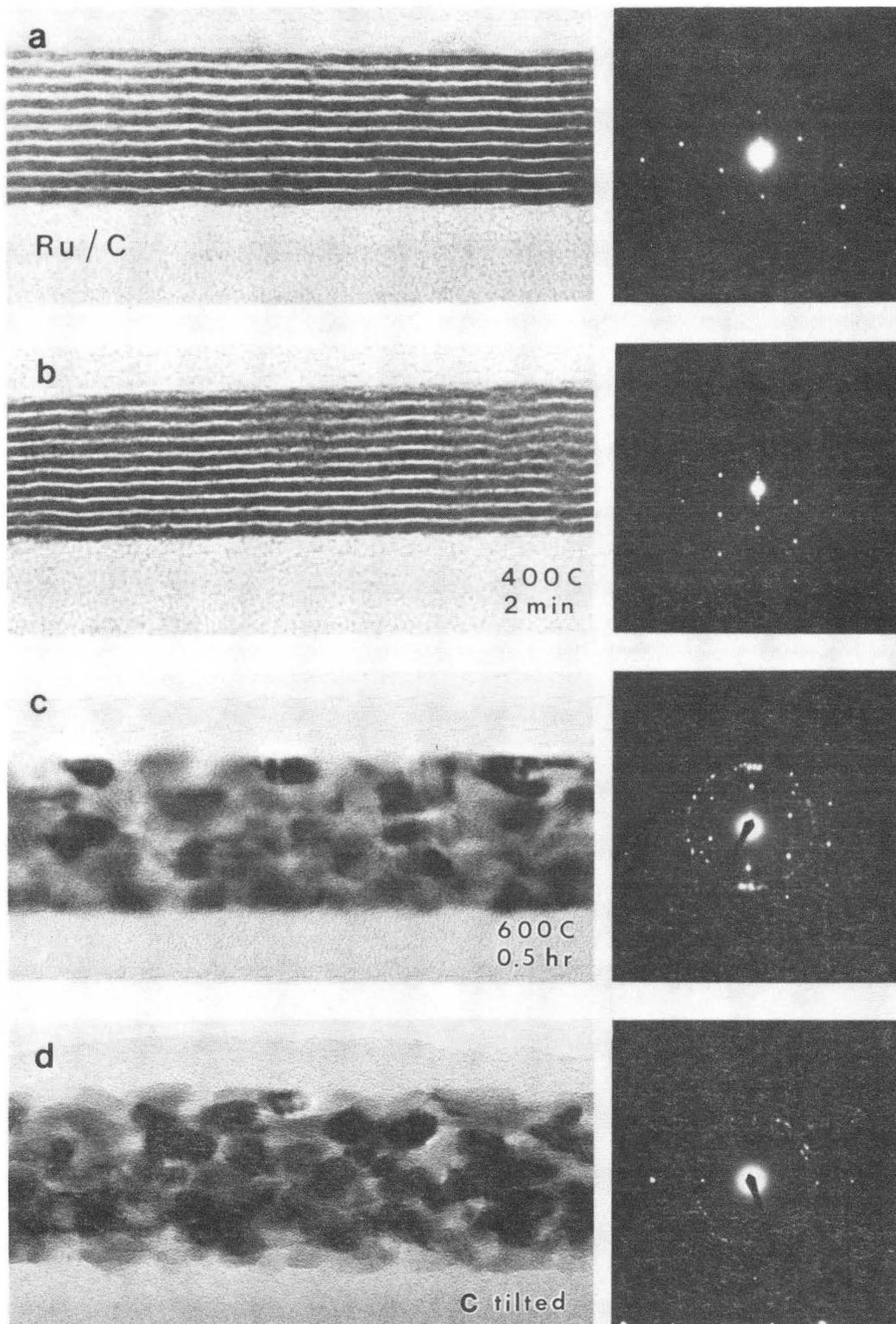
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Fig. 1 -- Plan-view TEM images of a) 1/2, b) 1/1, c) 1/0.5, d) 2/4, e) 2/2, f) 2/1, g) 4/8, h) 4/4, i) 4 nm Ru / 2 nm carbon multilayers after annealing at 800°C for 30 minutes. The electron diffraction patterns in j)-l) correspond to the bright field images in g)-i), respectively.



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Fig. 2 -- TEM images of as-prepared and annealed 1 nm Ru / 1 nm carbon multilayers: a) as-prepared, b) 400°C for 2 minutes, c) 600°C for 30 minutes, showing agglomeration in the Ru films, and d) sample in c) tilted perpendicular to the film surface to show the morphology and the crystallites and the interface.

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