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Electron Impact-Assisted Carbon Film Growth on Ru(0001): Implications for Next-Generation EUV Lithography

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Carbonaceous deposits produced on Ru-capped multilayer mirrors under extreme ultraviolet (EUV) irradiation in the presence of adventitious gaseous hydrocarbons are a major obstacle to process implementation of EUV lithography, the key to fabrication of next generation semiconductor chips. The technical problem has been simulated by examining graphitic film growth on Ru(0001) under low-energy electron irradiation in the presence of 1-butene, C5–C8 linear alkanes, and toluene. We show that this provides a practical and reliable means of simulating the photon-induced chemistry and of distinguishing between benign and harmful species. Linear alkanes up to *n*-heptane are relatively benign, whereas *n*-octane and toluene are much more harmful, giving rise to rapid growth of graphitic films of a thickness sufficient to seriously impair mirror reflectivity. 1-Butene exhibits behavior in between these extremes. These properties may be understood in terms of the surface residence lifetimes of the various adsorbates on graphitic surfaces.

The inexorable demand for ever-higher component densities on silicon wafers has pushed current photolithographic technologies to their limit. Accordingly, Intel's lithography road map proposes the use of extreme ultraviolet (EUV) radiation ($\lambda = 13.5$ nm) for fabrication of next generation semiconductor chips.¹ The associated optical system is complex and costly and key scientific and technological barriers must be overcome before this technology can be fully implemented. At EUV wavelength, light absorption by lens materials dictates that reflective rather than refractive optics have to be used. This calls for highly specialized multilayer mirrors consisting of alternating layers of Mo and Si. In the simplest arrangement, the terminating layer is Si² passivated by a layer of native oxide.³ However, such mirrors have an exceptionally low tolerance to contaminants present in the EUV process environment, which cause reflectivity loss. Because of the number of successive mirror elements present in the optical system, a 1% loss of reflectivity signifies the end of mirror life: an ~ 1 nm thick deposit of carbonaceous material is sufficient for such degradation to occur,⁴ and the industrial target calls for mirror lifetimes of the order of 30 000 h.² Clearly, minimizing the contamination rate is of paramount importance, and little or nothing is known about the associated fundamental mechanisms. Madey et al.⁵ have recently described and discussed in detail the role of adventitious water vapor in EUV mirror degradation. Here, we focus on another important aspect: the processes that lead to carbon deposition in the presence of hydrocarbons under EUV illumination.

Multilayer mirror lifetimes can be significantly extended by the introduction of an additional capping layer⁶ consisting of materials such as SiC, Si₃N₄, Pt, Ru, Pd, Rh.⁷ Of these, ruthenium appears to be the most promising material:⁸ a 5 nm Ru-capping layer increases mirror lifetime by a factor of ~ 40 with minimal effect on the overall reflectivity of the underlying Mo/Si multilayer structure. However, although Ru-capping inhibits Si oxidation it does not prevent carbon deposition. Our research in this field has two objectives: (i) to elucidate the processes that give rise to EUV-induced carbon contamination of Ru-capped mirrors (ii) to develop mitigation strategies that will enhance mirror lifetime. The present paper addresses the first issue.

A Ru(0001) single crystal was used to simulate the ruthenium-capped multilayer mirror surface, and the effect of EUV-induced secondary electron emission was simulated using electron irradiation of an appropriate kinetic energy. It is found that extensive carbon deposition occurs in the presence of low pressures of gaseous hydrocarbons under low-energy electron irradiation of the Ru surface: we concentrate on the multilayer regime because, as explained above, this is where reflectivity attenuation becomes significant. Moreover, it is the surface lifetime of the various hydrocarbon species on a graphitic adlayer that determines the rate of carbonaceous multilayer growth, a process responsible for mirror degradation.

Measurements were performed in an ultrahigh vacuum chamber operated at a base pressure of 5×10^{-10} mbar and were equipped with a quadrupole mass spectrometer, an Al/Mg VSW X-ray source anode, and a VSW HA100 concentric hemispherical analyzer with multichannel detector. X-ray photoelectron spectroscopy (XPS) measurements were performed using Mg K α radiation with a photoelectron exit angle of 45°.

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The Ru(0001) single crystal (10 mm diameter; thickness 0.5 mm) could be resistively heated to 1500 K with the temperature being monitored by means of a 95% W/5% Re–74% W/26% Re thermocouple. Cleaning of the crystal surface was achieved by cycles of Ar⁺ sputtering (1 keV, 4 μ A) followed by annealing at 1000 K. Electron irradiation was achieved by means of a simple normal incidence source consisting of a negatively biased filament and a Wehnelt cylinder with the sample held at ground potential. Quoted XPS binding energies are calibrated against the Ru 3d_{5/2} peak at 280.1 eV. The *n*-pentane (99+ %), *n*-hexane (99+ %), *n*-heptane (99+ %), *n*-octane (99+ %), and toluene (99.8%) were obtained from Sigma-Aldrich; 1-butene (99.9%) and *n*-butane (99+ %) were obtained from BOC Special Gases; propane (99.95%) was obtained from Messer Gases. These were delivered to the sample via a 6 mm diameter collimator tube. Reported pressures are corrected for molecular ionization cross sections and collimator gain factor. Synchrotron radiation measurements were carried out on the vacuum ultraviolet beamline at ELETTRA, Trieste, Italy.

Electron versus Photon Irradiation.

The photochemistry taking place on the mirror surface upon EUV irradiation can be induced in two distinct ways: (i) by direct photodissociation, that is, light absorption by the adsorbate resulting in electronic excitation and subsequent decomposition and (ii) by electron impact-induced adsorbate decomposition caused by photoemitted secondary electrons exiting the surface.⁵ The cross sections for direct photodissociation of organics on metal surfaces by incident photons are negligible in comparison to the molecular dissociation cross sections associated with resultant photoelectrons.⁹ In other words, it is the photoelectrons rather than the incident EUV radiation that cause adsorbate damage, as demonstrated by Boller et al.⁹ who studied the contamination of a gold-capped EUV mirror using synchrotron radiation.

The possibility of electron-induced dissociation of gaseous hydrocarbons followed by surface deposition of the resulting molecular fragments may be ruled out under the conditions used here (and in practical EUV systems). Such effects become appreciable only at pressures > 10^{−4} mbar as would be expected on the basis of the electron/molecule collision frequency and electron impact excitation/fragmentation cross sections in the order of 10^{−21} m² and confirmed experimentally by Poole.¹⁰ Consistent with this, synchrotron radiation studies by Rosenberg et al.¹¹ showed that surface contamination processes are dominated by surface reactions rather than gas-phase chemistry.

As discussed by Madey et al.,⁵ the surface chemistry of Ru and other metals can be strongly affected by the low-energy secondary electrons produced by any kind of ionizing radiation (photons, electrons, ions) incident on the surface. As noted above, the relatively high molecular excitation and dissociation cross sections characteristic of these electrons are the most probable cause of mirror degradation in the real process environment. Accordingly, using synchrotron radiation, we measured the photoelectron energy distribution resulting from irradiating Ru(0001) with 13.5 nm light (91.8 eV). As shown in the Supporting Information, this electron kinetic energy distribution could be simulated satisfactorily by using 87.5 eV incident electrons, which is the procedure we followed in subsequent laboratory experiments.

Hydrocarbon Uptake.

XPS observations of carbon-containing species on Ru surfaces are complicated by the overlap between C 1s and Ru 3d_{3/2}

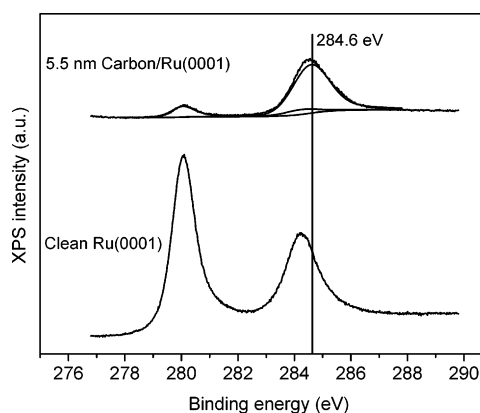


Figure 1. Ru 3d and C 1s XPS region of the clean Ru(0001) and after deposition of 5.5 nm carbon.

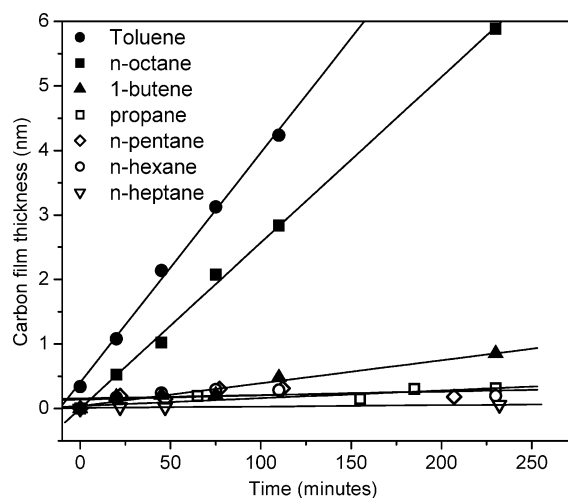


Figure 2. Electron-assisted uptakes of various hydrocarbons on Ru(0001) as monitored by XPS.

emission; however, carbon accumulation on Ru can be followed by monitoring the Ru 3d_{5/2}:3d_{3/2} intensity ratio. Exposure of Ru(0001) to 3.5×10^{-7} mbar toluene for 150 min under irradiation by 87.5 eV electrons (~ 2 mW/mm²) deposited multilayers of carbon on the surface, as illustrated in Figure 1, which shows Ru 3d and the C 1s emission from (a) clean Ru(0001) and (b) after the above treatment. It is apparent that the treatment results in attenuation of the Ru 3d_{5/2} (280.1 eV) and 3d_{3/2} (284.2 eV) intensities, while a new peak appears at a binding energy of 284.6 eV, which is characteristic of graphitic carbon.¹² On the basis of the attenuation of the Ru 3d_{5/2} signal ($I = I_0 \exp(-d/\lambda \cos\theta)$), the thickness of the carbon deposit is estimated as ~ 5.5 nm, using an inelastic mean free path value of 2.8 nm (Tanuma et al.)¹³ and assuming that a continuous graphitic multilayer of uniform thickness was formed (bulk density 2.26 g/cm³).

Using this procedure, the time dependence of electron-assisted carbon uptake by exposure to toluene, 1-butene, propane, *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane at 343 K was measured (Figure 2). These hydrocarbons are representative of the species encountered in typical vacuum process environments. It is apparent that toluene and *n*-octane contaminate the surface at a significantly higher rate than the linear alkanes up to and including *n*-heptane. Interestingly, the unsaturated species 1-butene contaminates the surface at a negligible rate, comparable to that observed for the shorter chain alkanes.

For toluene, Figure 3 illustrates the effect of hydrocarbon pressure on the rate of carbon accumulation for a fixed incident

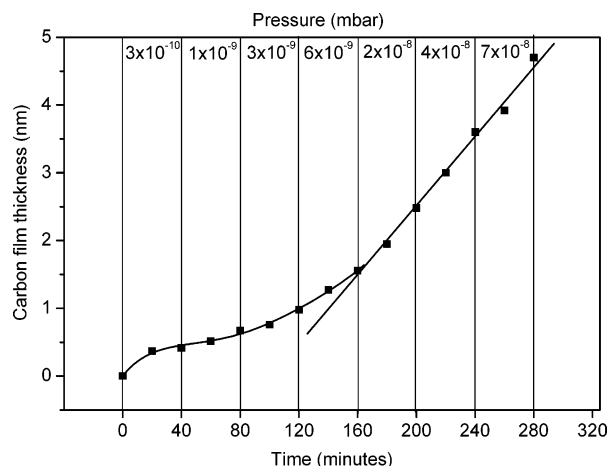


Figure 3. Effect of increasing the partial pressure of toluene on the rate of carbon accumulation for a fixed electron flux (87.5 eV, 2 mW/mm²).

electron flux of 1.8 mA at 87.5 eV. This corresponds to a power dissipation of ~ 200 mW at the sample that would cause a negligible temperature rise. Operating the electron source did, however, cause a small temperature increase (~ 40 K) above room temperature due to radiation from the filament. Control experiments with the filament on but emission suppressed by biasing the Wehnelt cylinder showed no detectable thermally driven carbon uptake; all the effects we report are electron-induced. The data were acquired by exposing the initially clean Ru surface to successively increasing pressures of toluene for 20 min intervals under a fixed electron flux of ~ 2 mW/mm², XP spectra being acquired after each dose. At 3×10^{-10} mbar toluene, initial carbon uptake occurred relatively rapidly up to a (nominal) film thickness of ~ 0.3 nm. This may be reasonably attributed to fast uptake of toluene on bare Ru sites, resulting eventually in a complete monolayer of graphitic carbon. Subsequent film growth then occurs by adsorption and electron-induced decomposition of toluene on the graphitized surface. In the regime 1×10^{-9} to 2×10^{-8} mbar, the carbon accumulation rate increases with toluene pressure; subsequently, it becomes invariant with hydrocarbon pressure. The implication is that a transition occurs between a low-pressure regime in which the impingement rate of molecules is rate-determining and a high-pressure regime in which the electron impingement rate becomes rate-determining.

Clearly, it is the adsorption properties of the various hydrocarbons on the graphite-covered Ru surface that determines the rate at which the optical properties of Ru mirrors are degraded; recall that significant reflectivity degradation sets in for contamination layer thicknesses > 1 nm. Accordingly, it is of interest to estimate the surface lifetimes of the various species on graphite surfaces at 343 K by use of the following equation:

$$\tau = \tau_0 \exp(-\Delta H_{\text{AD}}^0/RT)$$

where τ is the surface residence time, τ_0 is the vibrational period of the adsorbed molecule, ΔH_{AD}^0 is the enthalpy of physisorption, R is the ideal gas constant, and T is the temperature (343 K, which was the temperature of the substrate during the experiments). Gellman and co-workers have studied the desorption behavior of linear alkanes from graphite surfaces in detail, both experimentally and theoretically, so we may use their estimates of ΔH_{AD}^0 and τ_0 for pentane, hexane, heptane, and octane with confidence^{14,15} (no comparable data are available for toluene and 1-butene). Figure 4 shows a plot of

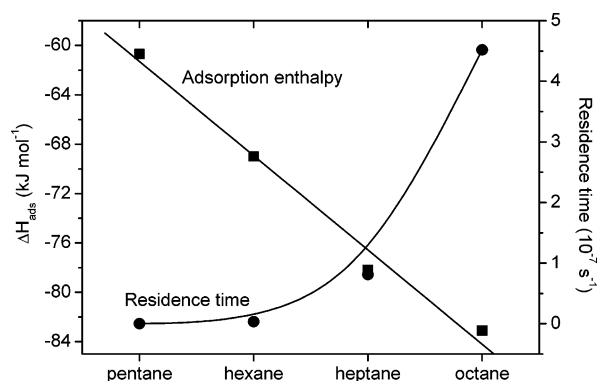


Figure 4. Residence times and adsorption enthalpies of *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane on graphite. ΔH_{AD}^0 data taken from refs 14 and 15.

the calculated adsorption enthalpies^{14,15} and the corresponding surface residence times for the C5–C8 linear alkanes. The linear dependence of ΔH_{AD}^0 on chain length results in a strong dependence of surface residence time on carbon number. This is in very good accord with the data presented in Figure 2, which show that electron impact-assisted carbon film growth on Ru(0001) is triggered when the *n*-alkane chain length reaches C8. In other words, we may infer from Figures 2 and 4 that under EUV process conditions C1–C7 alkanes may be regarded as relatively benign, whereas aromatics and alkanes $> \text{C8}$ are highly detrimental. It is interesting to note that small unsaturates (1-butene in our case) are relatively benign, confirming that carbon film growth occurs by electron impact decomposition of molecules adsorbed on a graphite surface. 1-Butene would be very “sticky” on bare Ru sites due to the chemical affinity provided by the C=C functionality. On graphite where the gas/surface interaction is dominated by van der Waals forces, the presence of a C=C function is not of overwhelming importance as it would be on a Ru (or Pt, Pd) surface; what matters most is the carbon number. However, the data in Figure 2 show that the C=C function does have some effect: 1-butene is measurably more harmful than C5, C6, and C7 alkanes.

Conclusions

1. Measurements on the behavior of hydrocarbons under low-energy electron irradiation in the presence of a Ru(0001) surface provide a practical and reliable means of simulating the photon-induced chemistry of ambient contaminants that impair the reflectivity of Ru-capped multilayer mirrors under EUV process conditions.

2. Linear alkanes up to *n*-heptane are relatively benign, whereas *n*-octane (and higher alkanes) and toluene are much more harmful, giving rise to rapid growth of graphitic films of a thickness sufficient to seriously impair mirror reflectivity. 1-Butene exhibits behavior inbetween these extremes.

3. These observations can be accounted for very satisfactorily in terms of the surface residence lifetimes of the various adsorbates on graphitic surfaces.

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Supporting Information Available: Comparison of secondary electron kinetic energy distributions resulting from irradiating Ru(0001) with (i) 91.8 eV photons (synchrotron) and (ii)

87.5 eV electrons. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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