

Photochemically Induced Metallization of Surface Silicon Using Dinuclear Metal Carbonyl Compounds. Anchoring of Ruthenium to a Si(111) Surface through Covalent Ru–Si Bond Formation

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Near-UV irradiation of hydrogen-terminated Si(111) wafers with the ruthenium–ruthenium bonded dinuclear compounds $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (where $\text{Cp} = \eta^5\text{-MeC}_5\text{H}_4$, $\eta^5\text{-C}_5\text{Me}_5$) and $[\text{HB}(\text{pz})_3]_2\text{Ru}_2(\text{CO})_4$ [where $\text{HB}(\text{pz})_3$ = hydrotris(1-pyrazolyl)borate] in benzene solution at room temperature leads to the covalent attachment of $\text{CpRu}(\text{CO})_2$ and $[\text{HB}(\text{pz})_3]\text{Ru}(\text{CO})_2$ moieties to surface silicon sites on the wafer. ATR FTIR, XPS, and RBS data support the proposed Ru–Si bond formation as the dominant mode of wafer metallization. The surface area coverage of these ruthenized wafers is limited by the size the mononuclear ruthenium moiety that is attached to the Si anchor. A plausible reaction sequence involving the photochemically generated ruthenium-centered radicals $\text{CpRu}(\text{CO})_2$ and $[\text{HB}(\text{pz})_3]\text{Ru}(\text{CO})_2$ that both activate the hydrogen-terminated Si(111) surface and combine with the resulting silicon radicals is presented and discussed.

Introduction

A single-crystal silicon surface that is terminated by dangling silicon atoms is highly reactive. Upon exposure to air, the dangling silicon atoms are quickly oxidized, leading to the formation of a thin oxide layer. The resulting native oxide, which typically exhibits dimensions on the order of 30–50 Å,¹ can be removed or etched with hydrofluoric acid. This HF etching process is well-established and generates a silicon surface that is terminated by hydrogen.² Such hydrogen-terminated Si surfaces are surprisingly stable toward air oxidation and organic oxidants in comparison to nonfunctionalized silicon surfaces.³ Combined with other elements, modified silicon surfaces play a vital role in the microelectronics and catalysis industries and in the fabrication of sensor devices. The contemporary interest in processes and devices derived from modified-silicon surfaces requires the controlled introduction of surface-bound functionalities, with metallization of silicon representing one of the more strategically important industrial goals.⁴ Here both physical

(i.e., thermal or sputtering depositions) and chemical (i.e., electroplating or chemical vapor deposition) methods have been extensively used in the construction of metal microstructures having stringent dimensional or low-tolerance requirements. As the miniaturization trend in the microelectronics industry continues, the precise control of metallization on silicon in the nanometer domain is imperative.

A wide range of silicon surface modifications has been proposed and studied. The vast majority of the examples dealing with Si surface functionalization involves either hydrosilylation or alkylation reactions, whereby alkyl and alkyl-related moieties are anchored to the Si surface by adsorption or direct covalent bonding with silicon atoms.⁵ In this paper, we report our strategy to anchor organometallic ruthenium species on H-terminated silicon through strong Ru–silicon covalent bonds. Our selection of organo-transition-metal ruthenium complexes was based, in a large part, due to the current interest in ruthenium metal in the

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microelectronics field and catalytic fuel cells.⁶ If ruthenium metal in the form of a well-behaved and easily introduced organometallic precursor can be selectively and strongly tethered to a crystalline Si surface, one may envision a sequence whereby the ancillary ligands associated with the original ruthenium center are expelled, leading to metallization of the Si surface under mild reaction conditions. Several dinuclear ruthenium carbonyl complexes were examined for their ability to functionalize hydrogen-terminated Si(111) surfaces. Optical excitation within the $\sigma \rightarrow \sigma^*$ manifold belonging to the metal–metal bond in $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (where $\text{Cp} = \eta^5\text{-MeC}_5\text{H}_4$, $\eta^5\text{-C}_5\text{Me}_5$) and $[\text{HB}(\text{pz})_3]_2\text{Ru}_2(\text{CO})_4$ [where $\text{HB}(\text{pz})_3 = \text{hydrotris}(1\text{-pyrazolyl})\text{borate}$] leads to homolytic cleavage of the Ru–Ru bond and production of the reactive ruthenium-centered radicals $\text{CpRu}(\text{CO})_2$ and $[\text{HB}(\text{pz})_3]\text{Ru}(\text{CO})_2$.^{7,8} The surface modification process has been studied by total internal reflection FTIR, X-ray photoelectron spectroscopy (XPS), and Rutherford backscattering spectrometry (RBS). The Ru–silicon bond is relatively stable toward air oxidation, and our data suggest that the steric properties of the surface-bound $\text{LRu}(\text{CO})_2$ [where $\text{L} = \text{Cp}$, $\text{HB}(\text{pz})_3$] entities strongly influence the degree to which the Si surface is covered.

Experimental Section

General Procedures. The ruthenium compounds $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (where $\text{Cp} = \eta^5\text{-MeC}_5\text{H}_4$, $\eta^5\text{-C}_5\text{Me}_5$) were prepared from $\text{Ru}_3(\text{CO})_{12}$, which was synthesized from hydrated RuCl_3 according to carbonylation procedure of Bruce et al.,⁹ and the appropriate cyclopentadiene,¹⁰ while $[\text{HB}(\text{pz})_3]_2\text{Ru}_2(\text{CO})_4$ was synthesized from RuO_2 and potassium hydrotris(1-pyrazolyl)borate.¹¹ The benzene employed in the photolysis studies was distilled from sodium/benzophenone under argon and stored in Schlenk flasks equipped with high-vacuum Teflon stopcocks.¹² All other organic solvents were of reagent grade and used directly without further purification. All reagents utilized in the cleaning and preparation of silicon wafers were of semiconductor grade without exception. The ultrapure water (UPW) used in the preparation of the hydrogen-terminated Si(111) wafers was obtained from a Millipore Milli-Q Elix 5 purification system (Millipore Corp., Bedford, MA), which supplied UPW having a resistance greater than 18.2 M Ω . N-type, (111)-oriented single-crystal silicon wafers were purchased from Polishing Corporation of America, CA. The near-UV irradiation source utilized in all photochemical experiments consisted of two parallel GE black light bulbs having a maximum output of 366 nm.

The routine IR spectra of the starting ruthenium carbonyl complexes $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ and $[\text{HB}(\text{pz})_3]_2\text{Ru}_2(\text{CO})_4$ were recorded on a Nicolet 20SXB FTIR spectrometer in 0.1 mm NaCl cells. All multiple internal reflection infrared spectra (MIRIS) were recorded on a Bruker Equinox 55 system equipped with a high D*, narrow band MCT detector. The Si(111) ATR crystal was held in place in the FTIR chamber using a Pike Technologies variable angle ATR accessory, and the incident IR beam was focused normal to the bevels of the ATR crystal. The MIRIS spectra were recorded at 2.0 cm^{-1} resolution and were referenced to a clean silicon oxide surface as the background. The X-ray photoelectron spectroscopic data were obtained from a Thermo VG Scientific ESCALAB MKII spectrometer system using a standard Al–K α X-ray source at 280 W and electrostatic analysis in constant pass energy mode of 200 eV for survey scans and 20 eV for regional scans. The coverage of ruthenium on the silicon wafer was determined by Rutherford backscattering spectrometry (RBS), using a NEC 9SDH Pelletron accelerator. The RBS data analysis employed a 0.5 MeV He⁺ beam incident normal to the sample surface, with a scattering angle of 168° and a detection solid angle of 1.14×10^{-3} msr. The absolute measurement of the number of ruthenium atoms per unit area was determined by using the area under the RBS ruthenium peak, as per the surface approximation method.¹³ The absolute measurements were determined with an uncertainty of 6%, utilizing a mesh-based charge integration procedure¹⁴ in conjunction with a RBS standard.

Preparation of the Monohydride-Terminated Si(111) Wafers.

In a typical preparation, a Si(111) wafer having dimensions of 1.0 cm \times 6.0 cm \times 0.7 cm and possessing bevels that were mirror polished with a bevel angle of 45° was employed in the surface functionalization studies. The ATR element prepared in this fashion allows up to 86 internal reflections to be collected for each face of the crystal. Standard SC2 (hot solution of 1:1:5 ratio of H_2O_2 :HCl:H₂O) and SC1 (1:1:5 ratio of H_2O_2 : NH_4OH :H₂O) cleaning procedures were adopted in the cleaning of the surface of the silicon wafer. Each hot cleaning step was followed by 4.9% HF etching and rinsing with ultrapure water. A uniform monohydride-terminated silicon surface was next achieved by dipping the cleaned, HF-etched ATR element in buffered HF (pH \sim 9.2) for 9 s,^{2a,15} followed by rinsing with ultrapure water and purge drying under nitrogen gas. From this point on, the ATR crystal was manipulated with aid of Teflon tweezers.

Photochemical Activation and Binding of the Ruthenium Carbonyl on the H-Terminated Silicon Surface. To a small Schlenk vessel containing the Si(111) ATR crystal was added 15 mL of a benzene solution containing the ruthenium dimer (ca. 10^{-3} M) under argon flush. The solution was then freeze–pump–thaw degassed three times prior to photolysis at room temperature. After the reaction was terminated, the ATR crystal was removed and sonicated in CH_2Cl_2 for 10–15 min to remove any residual metal carbonyls associated with the silicon surface. The ATR crystal was next rinsed twice with CH_2Cl_2 /benzene and dried under a purge of nitrogen gas.

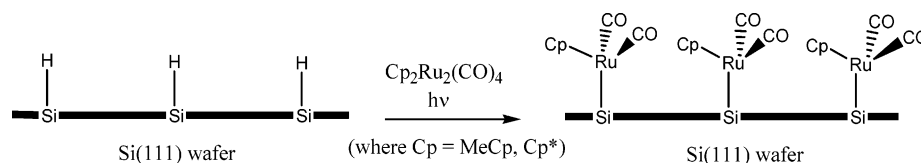
Results

Si(111) Wafer Stability Studies. The silicon oxide surface that is generated from the SC1 cleaning procedure is readily transformed to the monohydrogen-terminated Si(111) wafer upon treatment with buffered HF. Short exposure times afford

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Scheme 1



uniform and specific monohydrogen coverage of the wafer surface, where the Si–H bonds are oriented normal to the Si(111) surface plane.^{15,16} The characteristic $\nu(\text{Si–H})$ stretches at 2083 and 2071 cm^{-1} are ascribed to the symmetric and antisymmetric stretching modes, respectively, for the kinematically coupled surface monohydride groups.¹⁵ The passivated Si(111) surface was found to be stable toward near-UV irradiation at 366 nm in benzene solvent for a period of at least 24 h, as evidenced by FTIR and XPS data that confirmed the absence of any surface oxide. These experiments corroborate the earlier results of Chidsey and co-workers that showed wavelength-dependent photochemistry.^{5g} There the overall composition of the surface hydrogen on Si(111) wafers was shown to exhibit no gross alteration of structure upon photolysis with light using wavelengths longer than 300 nm in the presence of atmospheric oxygen.

Surface Ruthenation of the Si(111) Wafer. Photolysis of a benzene solution containing the diruthenium compounds $\text{Cp}_2\text{Ru}_2(\text{CO})_4$ (Cp = MeCp, C_5Me_5) in the presence of a monohydrogen-terminated Si(111) wafer for 24 h at room temperature leads to the complete consumption of the pendant monohydride ligands and attachment of $\text{CpRu}(\text{CO})_2$ moieties, as illustrated in Scheme 1. The formation of $\text{CpRu}(\text{CO})_2\text{H}$ accounts for fate of the surface hydrogen atoms.

Proof for the successful ruthenation of the silicon wafer was initially obtained by FTIR spectroscopy. Figure 1 gives the ATR FTIR spectral data for both of the cyclopentadienylruthenium-functionalized wafers in the carbonyl region, with the IR spectrum of the starting hydrogen-terminated Si(111) wafer displayed underneath for comparative purposes. Here the functionalized wafer using the MeCp

derivative affords two moderately intense $\nu(\text{CO})$ bands at 2015 and 1970 cm^{-1} belonging to the silicon-tethered species $\text{MeCpRu}(\text{CO})_2(\text{Si surface})$. The two terminal ruthenium carbonyl stretching bands observed are reminiscent of the A' and A'' vibrations reported for simple cyclopentadienyl compounds $\text{CpM}(\text{CO})_2\text{X}$ (where M = Fe, Ru, Os; X = halides, CN, acetyl, SnCl_3).¹⁷ The observed frequency for the $\nu(\text{CO})$ bands in the surface-ligated $\text{MeCpRu}(\text{CO})_2$ entities are in excellent agreement with those data reported by Pannell et al. for the silane-substituted compounds $\text{CpRu}(\text{CO})_2\text{SiMe}_3$ and $\text{CpRu}(\text{CO})_2\text{Si}_n\text{Me}_x$ (where $n = 2, x = 5$; $n = 3, x = 7$) strongly supporting the attachment of $\text{MeCpRu}(\text{CO})_2$ moieties to the exposed silicon atoms on the surface of the wafer through a strong Ru–Si covalent bond.¹⁸ Integration of the intensity of two $\nu(\text{CO})$ bands at 2015 and 1970 cm^{-1} allows for the calculation of the angle subtended by the two CO groups and the ruthenium center.¹⁹ Here an angle of 98° is computed, which is consistent with a three-legged piano stool complex of the form $\text{MeCpRu}(\text{CO})_2(\text{Si wafer})$. Use of the pentamethylcyclopentadienyl complex $\text{Cp}^*\text{Ru}_2(\text{CO})_4$ yields the corresponding functionalized wafer containing $\text{Cp}^*\text{Ru}(\text{CO})_2$ units. The IR spectrum of the wafer reveals two $\nu(\text{CO})$ bands at 2006 and 1958 cm^{-1} . The shift to lower frequency of the two carbonyl stretching bands vis-à-vis the monomethyl analogue $\text{MeCpRu}(\text{CO})_2$ is in accord with the increased electron density at the ruthenium center. Moreover, the observed $\nu(\text{CO})$ frequencies for the $\text{Cp}^*\text{Ru}(\text{CO})_2(\text{Si wafer})$ moieties are in excellent agreement with the IR data for the silyl-substituted compounds $\text{Cp}^*\text{Ru}(\text{CO})_2(\text{SiR}_3)$.²⁰ Finally, the OC–Ru–CO bond angle in the $\text{Cp}^*\text{Ru}(\text{CO})_2(\text{Si wafer})$ species has been calculated as 94°. This angle supports the existence of a six-coordinate ruthenium atom and is consistent with the proposed structure of the surface-bound species that possesses a $\text{Ru}(\text{CO})_2$ moiety with two mutually cis CO groups.

Additional verification for the modification of the wafer surface and determination of the oxidation state for the surface-bound ruthenium derive from XPS analysis, as shown in Figures 2 and 3 of the MeCp derivative. Since the signals

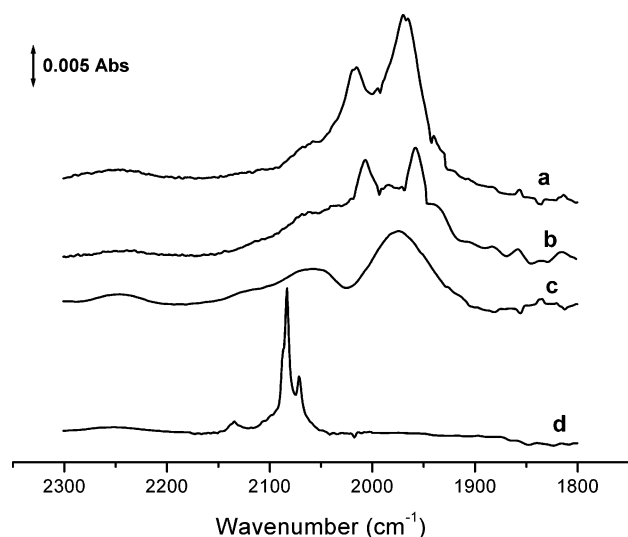


Figure 1. ATR FTIR spectra for the ruthenium-functionalized Si(111) wafers and the monohydride Si(111) starting wafer: (a) $\text{MeCpRu}(\text{CO})_2$ -(Si-wafer), (b) $\text{Cp}^*\text{Ru}(\text{CO})_2$ -(Si-wafer), (c) $[\text{HB}(\text{pz})_3]\text{Ru}(\text{CO})_2$ -(Si-wafer), and (d) hydrogen-terminated Si(111) wafer.

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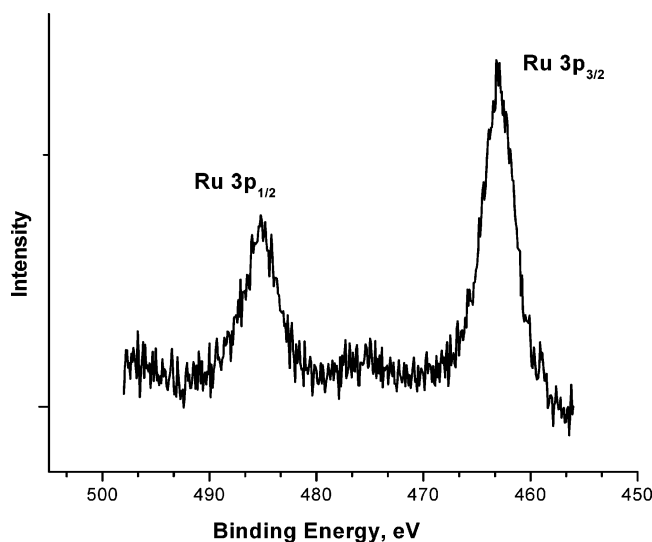


Figure 2. X-ray photoelectron spectrum of the Si(111)-bound MeCpRu(CO)₂ moiety showing the Ru 3p signals.

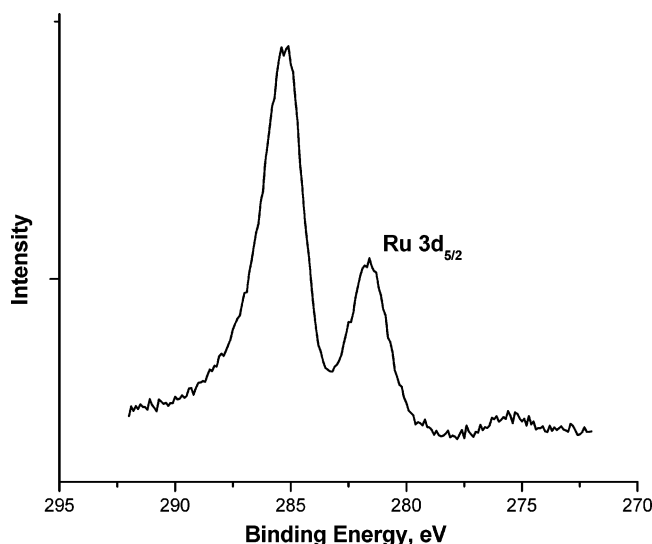


Figure 3. X-ray photoelectron spectrum of the Si(111)-bound MeCpRu(CO)₂ moiety showing the Ru 3d signals. The Ru 3d_{3/2} signal at ca. 285 eV also contains C 2s contributions from the MeCp and CO ligands and atmospheric carbon impurities.

from the C(1s) and Ru(3d_{3/2}) ionizations exhibit substantial overlap, we have utilized the Ru(3d_{5/2}), Ru(3p_{3/2}), and Ru(3p_{1/2}) signals that have been found at 281.5, 463.0, and 485.0 eV, respectively, for the MeCpRu(CO)₂(Si wafer) sample. The value found by us for the Ru(3d_{5/2}) signal here agrees well with the data reported by Gassman and co-workers for a series of ruthenocene derivatives and indicates that the ruthenium is present in the (+2) valence state.^{21,22} A formal oxidation state of (+2) is anticipated for the ruthenium atom in a covalently bound surface entity

CpRu(CO)₂(Si wafer), as dictated by rules governing conventional oxidation state formalism.²³ The XPS spectrum of the MeCpRu(CO)₂(Si wafer) in the silicon 2p region shows the presence of silicon oxide at 103.0 eV that helps account for the diminution of the surface Si–H coverage, as evidenced in the IR spectrum of the same sample (vide supra). The surface oxide is presumed to derive from adventitious oxygen and/or liberated CO.²⁴

We have also examined the reactivity of the related diruthenium complex [HB(pz)₃]₂Ru₂(CO)₄ [where HB(pz)₃ = hydrotris(1-pyrazolyl)borate] with hydrogen-terminated Si(111) wafers. This particular complex contains a tris-(pyrazolyl)borate ligand that is isolobal with its cyclopentadienyl counterparts MeCp and Cp*,²⁵ and as such, analogous Si(111) surface functionalization is expected, with the advantage of providing additional spectroscopic signatures unique only to the ancillary tris(pyrazolyl)borate moiety. Room temperature photolysis at 366 nm of a benzene solution containing [HB(pz)₃]₂Ru₂(CO)₄ and Si(111) wafers for 24 h led to the functionalization of the silicon surface by [HB(pz)₃]Ru(CO)₂ moieties, as shown in Scheme 2.

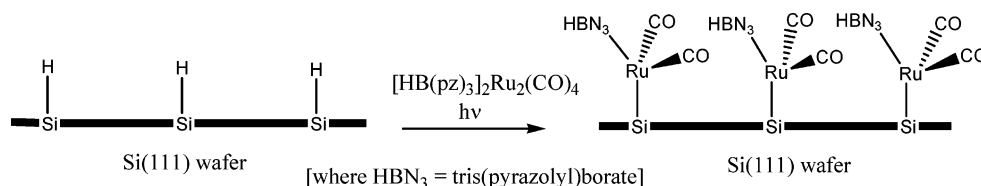
The IR spectrum of the [HB(pz)₃]Ru(CO)₂–silicon substituted wafer (Figure 1c) displayed two terminal carbonyl stretching bands at 2070 and 1990 cm^{−1} that are lower in frequency in comparison to the corresponding chloro complex [HB(pz)₃]Ru(CO)₂Cl, which exhibits ν(CO) bands at 2074 and 2012 cm^{−1}.¹¹ The computed OC–Ru–CO bond angle in the surface-bound complex is 89° in good agreement with an octahedral ruthenium center. Moreover, our finding that this angle is slightly smaller than the measured angle in the MeCp and Cp* derivatives is in accord with the fact that the HB(pz)₃ ligand is sterically larger than either of the two Cp ligands, manifesting itself in a congested ruthenium center and contraction of the OC–Ru–CO bond angle.²⁶ A ν(B–H) stretch at 2448 cm^{−1} unequivocally demonstrates the presence of the HB(pz)₃ moiety in the silicon-tethered ruthenium species. XPS analysis revealed characteristic nitrogen and boron 1s signatures at 401.0 and 190.0 eV, respectively,²⁷ along with Ru(3d_{5/2}), Ru(3p_{3/2}), and Ru(3p_{1/2}) signals at 281.5, 463.0, and 485.0 eV, respectively, that nicely match those data found by us for the MeCpRu(CO)₂(Si wafer) complex.

Monolayer Composition. The surface coverage of the Si(111) wafer by MeCpRu(CO)₂ and [HB(pz)₃]Ru(CO)₂

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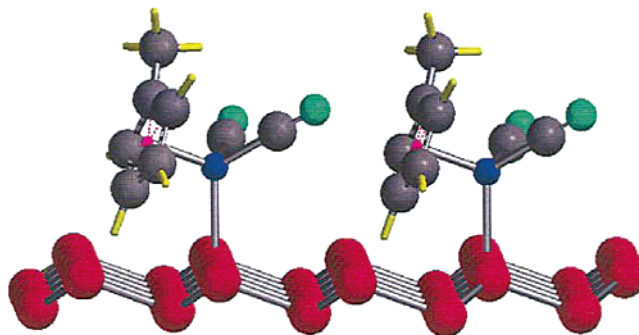
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Scheme 2



moieties was next evaluation by Rutherford backscattering spectrometry (RBS), with Figure 4 showing the RBS data. Our first task was to compute a reasonable theoretical coverage ratio of the wafer with the ruthenium compounds employed and establish an upper or maximum limit for the Ru:Si ratio in a monolayer. The number of potential hydrogen-terminated silicon sites available on the Si(111) wafer for surface functionalization is estimated at ca. 7.83×10^{14} silicon atoms/cm², and the maximum number of ruthenium units that may theoretically be accommodated by the silicon surface was arrived at by using the available X-ray structural data on the mononuclear compounds CpRu(CO)₂Br²⁸ and [HB(pz)₃]Ru(CO)(PPh₃)Cl.²⁹ Unfortunately, the solid-state structures for silyl-substituted compounds MeCpRu(CO)₂(SiR₃) and [HB(pz)₃]Ru(CO)₂(SiR₃) have either not been synthesized or structurally determined, requiring the use of closely related derivatives. In the case of the cyclopentadienyl complex CpRu(CO)₂Br, we replaced the bromine with a silicon atom and proceeded to measure the longest interatomic distance separating the mutually trans Cp group and CO ligand, whose distance was inflated by 10% to account for the presence of the ancillary methyl group in the MeCpRu(CO)₂. This method affords a working diameter for an assumed spherical MeCpRu(CO)₂ moiety of 6.41 Å, from which the effective number of ruthenium atoms/cm² can be estimated as 3.1×10^{14} , leading to a Ru:Si coverage ratio of ca. 0.4. This ratio of silicon to ruthenium is in excellent agreement with value of ca. 0.33 that we obtained by RBS analysis.³⁰ The X-ray data from the tris-(pyrazolyl)-substituted derivative [HB(pz)₃]RuCl(CO)(PPh₃) enabled us to measure directly an 8.2 Å interatomic distance between the pyrazolyl ring that is trans to the CO ligand. Using 4.1 Å as an effective radius for our surface-bound [HB(pz)₃]Ru(CO)₂(Si wafer) gives rise to a computed value

of ca. 1.90×10^{14} ruthenium atoms/cm² and a maximum Ru:Si ratio of ca. 0.24 that is in perfect agreement with the RBS-derived value of 0.22 for the wafer coverage by [HB(pz)₃]Ru(CO)₂. The representation depicts the MeCpRu(CO)₂ coverage of the Si(111) surface:



Silicon Metallization Mechanism. Near-UV photolysis of the diruthenium compounds Cp₂Ru₂(CO)₄ and [HB(pz)₃]₂Ru₂(CO)₄ in benzene solution leads to the disruption of the initial ruthenium dimer and production of the ruthenium-centered radicals CpRu(CO)₂ and [HB(pz)₃]Ru(CO)₂ due to population of the Ru–Ru σ* orbital.^{7,8,31} The resulting ruthenium radicals are pivotal in the activation of the protective hydrogen layer associated with the Si(111) surface by hydrogen atom abstraction, which in turn produces reactive silicon radicals and the corresponding ruthenium hydrides CpRu(CO)₂H and [HB(pz)₃]Ru(CO)₂H.³² The transient silicon radicals are then free to participate in a radical combination reaction with the ruthenium-centered radicals, whose concentration far exceeds that of the surface silicon radicals, or react with adventitious oxygen. This scenario readily accounts for formation of the observed surface-anchored ruthenium species CpRu(CO)₂ and [HB(pz)₃]Ru(CO)₂ and the surface oxide that accompanies these reactions. The removal of the hydrogen covering that protects the Si(111) wafer by the ruthenium radicals must be extremely efficient as no residual monohydride is observed on the surface of the ruthenated wafers by IR spectroscopy.

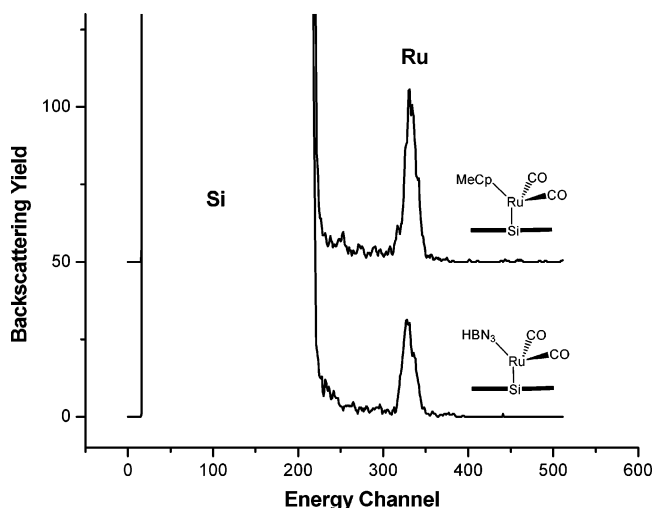


Figure 4. Normalized Rutherford backscattering spectra of Si(111)-bound MeCpRu(CO)₂ and [HB(pz)₃]Ru(CO)₂ moieties.

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Conclusions

We have demonstrated the functionalization of H-terminated Si(111) surfaces by using photosensitive dinuclear ruthenium compounds. Photochemical generation of reactive ruthenium-centered radicals under mild conditions leads to the removal of the protective hydrogen layer of the Si(111) wafer, followed by radical combination of the surface silicon and solution ruthenium radicals, to furnish the ruthenium anchored species $\text{CpRu}(\text{CO})_2(\text{Si wafer})$ and $[\text{HB}(\text{pz})_3]\text{Ru}(\text{CO})_2(\text{Si wafer})$. The functionalized silicon wafers have been characterized by ATR FTIR spectroscopy, and XPS and RBS methodologies, and the data support the fact that the ruthenium complexes are covalently bound to the surface of

the Si(111) wafer. Our future efforts will concentrate on defining the generality associated with the free-radical promoted metallization scheme employing homonuclear and mixed-metal cluster compounds. The resulting silicon-tethered metal clusters will be studied for their catalytic activity and as precursors for the facile introduction of zero-valent metal(s) on the silicon surface.

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