Compact plasma source for removal of hydrocarbons for surface analysis

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A low–energy, constricted-anode Anders-type plasma source was built and tested for the chemical removal of adventitious carbon on surfaces. Oxygen plasma, generated in the source, extends to the sample surface through an aperture in the anode. This plasma reacts with surface hydrocarbons and removes them in less than a minute without influencing the intrinsic surface stoichiometry of nonoxidizing samples such as minerals, glasses, and metal oxides. Adventitious carbon removal is critical for accurate binding energy determination and quantitative measurements in XPS and AES, particularly in multicomponent materials. We measure the plasma to be composed primarily of O+ and O2+, with minor H+, H2+, and O2++ components. Ion energy distributions were measured for O+ and O2++ and show all emitted ions have energies less than 50 eV, confirming chemical desorption as the primary removal mechanism. The plasma source, easily built ‘in house’, is compact and can be mounted on a 2.75-in flange for in situ specimen cleaning prior to surface analysis. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: adventitious carbon; plasma; plasma cleaning; plasma source; hydrocarbons; sample cleaning

Introduction

Adventitious carbon is a ubiquitous feature of surface analytical spectra – appearing in XPS, AES, and SIMS. These carbonaceous deposits exist on all surfaces exposed to the atmosphere and are thought to be a type of hydrocarbon contamination, based on the binding energy of the carbon 1-s photoelectron peak, ~285.0 eV, measured on conductive surfaces. This layer of surface carbon, which can be a fraction of a monolayer to several monolayers in thickness, forms in islands on sample surfaces, attenuating signal from the specimen.[1] The adventitious carbon layer occurs always on the outermost surface of materials. While adventitious carbon does not generally bond chemically to the surface, it adds error to the quantitative calculation of concentration for intrinsic surface elements and obscures signal due to trace elements and impurities.[2]

However, the ubiquitous nature of adventitious carbon has also made it an attractive standard to use as a binding energy reference for nonconductive samples; researchers fix the spectral binding energy scale by shifting the entire spectrum such that the primary carbon peak sits at a given binding energy value, typically 284.8 ± 0.2 eV.[3] The spread in binding energy is known to vary with the amount of carbon on the surface and the substrate material to which it adheres, limiting the accuracy of the energy scale.[3] Adventitious carbon is recommended as a binding energy standard only in cases where no better standard is available or the absolute binding energy measurement is unimportant.[4]

A number of techniques have been employed to remove adventitious carbon from samples: solvent baths, chemical etching, sputter cleaning, heating, and ex situ plasma etching.[5] Each of these removal techniques is helpful under specific conditions, but ex situ carbon removal does not eliminate carbon redeposited between the cleaning process and insertion into the analysis vacuum chamber, and chemical etching often introduces surface impurities from etchant residue. The most common in situ technique, sputtering, is typically done in an analysis or preparation chamber with keV Ar ions; however, sputtering produces atomic layer mixing and preferential element removal. Heating to temperatures required for hydrocarbon removal (~400 °C) is not an option for polymers or many samples with mobile or thermal segregating elements. Thus, a technique to remove adventitious carbon that can be mounted on the analysis chamber and produces no damage or impurities would be useful, as well as unique.

Description of Constricted-Anode Plasma Source

Low-pressure plasmas are nearly neutral mixtures of neutral atoms and molecules, excited neutrals, low-energy ions and electrons. They are formed in a gas when a sufficiently high voltage is applied between two metal electrodes, cathode and anode. While the peak of the electron energy spectrum lies below the ionization or dissociation energies of gas-phase molecules, the tail of the distribution lies above. It is these higher energy (>50 eV) electrons that generate the plasma as they collide, ionizing and exciting atoms as well as forming radicals. The lower energy electrons are contained within the plasma by the plasma sheath, which forms between the walls of the cathode and the higher potential plasma. Plasma sources are defined by their method of generation, pressure, ion and electron energy, composition, and density.[6]

To remove the adventitious carbon from mineral samples, we constructed a constricted-anode plasma source based on a design developed by Anders at Lawrence Berkeley National Laboratory.[7–9] Anders’ design features a d.c. glow discharge tube with a small aperture in the anode, which serves as a nozzle through which the plasma flows outward. The unique...
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quality of this plasma source is that the majority of the ions have low energies, at or below the sputtering threshold. This low energy occurs when an insulator with a very small aperture is used to separate the anode from the cathode, thus effectively reducing the size of the anode and increasing the current density at the ‘reduced’ anode. A low-voltage, double-layer virtual anode forms on the cathode side of the insulating aperture.[7–11] Ions emitted from this high-density region have a kinetic energy similar to the potential of the virtual anode. In addition, recent experiments have shown that an even lower energy spectrum (<20 eV) may be obtained by floating, rather than grounding, the anode electrode.[9]

Our constricted-anode plasma source was designed specifically to provide low-energy oxygen ions to a sample with superficial hydrocarbon contamination. The oxygen ions react chemically with the hydrogen and carbon on the surface and selectively remove surface hydrocarbon and organic contamination. This occurs without disturbing the native specimen, except in oxidizing samples such as pure metals and metal alloys where a thin metal oxide grows in response to the oxygen gas in the plasma source. In addition, we required a source that could be easily mountable on a ultra-high vacuum (UHV) vacuum chamber, for in situ cleaning, and fit on a standard 2.75-in conflat flange through a stainless steel tube (inner diameter (ID) 1.35”).

The plasma source, sketched in Fig. 1, consists of a copper support cup mounted by two aluminium legs attached to the conflat flange. The flange has three colinear liquid/gas feedthroughs welded through it: two for water cooling and a single center tube for gas admission. The source is cooled by water flowing through a copper tube wound around the copper cup and braised in place for maximal heat transfer. The water lines are fixed to the two water feedthroughs in the mounting flange using VCR® fittings. Inside the copper cup sits a second cup machined from BN, which electrically isolates the cathode from the grounded copper cup, and then an aluminum cup that serves as a cathode. A Kapton-coated copper wire, inserted through an aligned hole in the copper and insulating cups, delivers high voltage to the cathode and connects to the cathode cup via a small set screw. This screw is accessed through an aperture in the two outer cups. The cathode wire is connected to an electrical feedthrough on an auxiliary flange. Oxygen gas is fed from outside vacuum through a quartz capillary (ID ∼1 mm) to the cathode chamber. The cathode is then capped by an insulating disc (BN) with an aperture of 2 mm in it and then an aluminum disc (anode) with a 1-mm orifice which serves as an exit for the plasma.

A single power supply (1 kV; 30 mA) is required to provide voltage to the cathode. This supply is used in series with a current limiting 18 kΩ power resistor and an ammeter to quantify the emission current. The discharge voltage is measured directly between the cathode and the grounded anode.

To ignite the source, we flow O2 gas through the quartz capillary tube, and its pressure is controlled with a leak valve between the gas bottle and the capillary tube. At a pressure of ∼5 Torr and an applied voltage of ∼750 V, a glow discharge ignites and the cathode voltage drops to about a half. The green discharge can also be observed with the unaided eye (Fig. 2). Once the plasma starts, both the pressure and the power supply voltage can be reduced, resulting in a stable discharge current of ∼20 mA. Our standard running discharge voltage was approximately ∼350 V at a pressure ∼2 Torr measured on the capillary tube. However, the source will operate in a stable manner at pressures between 200 mTorr and >5 Torr which has a strong influence on the discharge parameters and output current.

Plasma Characterization

The plasma source was characterized using a Hiden Analytical Inc. EQS300 with energy analyzer to determine the ionic composition of the plasma, as well as the ion energy distribution. The source was located in line about 30 cm from the entrance aperture of the mass/energy analyzer. The ion mass spectrum was taken at four ion energies: 5, 10, 25, and 50 eV (Fig. 3), using an electrostatic energy filter at the entrance to the mass spectrometer. The oxygen plasma contains roughly equivalent amounts of O+ and O2+ ions, with O+++, H+, and H2+ as minor (<7%) components. No unexpected impurities are apparent, ensuring no spurious material is deposited on the sample surface during plasma etching. The hydrogen in the plasma is likely from absorbed water in the BN insulating disc which, according to manufacturer specifications, contains 0.5–3.0% water.

The total plasma current was measured on a copper collector plate at ∼10 cm in front of the source anode. We determined the positive component (ions) by deflecting the electrons away from the plate with a magnet and measuring the positive plate current with a Keithley 610B electrometer. We measured an ion current of 0.7 mA at the source conditions specified above.

It is important to identify the energy of the ions to ascertain the nature (physical or chemical) of the hydrocarbon removal.
the peak energy, and increase the O ion species, energy, or intensity. Lower pressure and reduced voltage changes the energy distribution of ions and their absolute materials. Adjusting the capillary pressure and cathode supply about 3 eV for atomic oxygen (10 eV for molecular oxygen), an below typical knock-on sputtering thresholds, with a small tail see that 95% of the oxygen ions have energies of less than 40 eV, ions: atomic and molecular oxygen. From the results in Fig. 4, we measure the performance of the plasma source with respect to hydrocarbon removal. The ability of the constricted-anode plasma source to remove adventitious carbon from the surface of a silicon wafer is shown in Fig. 6. The silicon wafer, stored in atmosphere, was analyzed by XPS and found to bear thin oxide with 15.8% (atomic percent) surface carbon. A subsequent exposure to the oxide plasma for 5 s removes the carbon to a level of 1.8%. Additional exposure to the oxide plasma reduces this C only slightly further, never completely eliminating it. We attribute this to redeposition of hydrocarbons desorbed from the walls of our unbaked preparation chamber. High resolution spectra (Fig. 6, inset) show in detail the increase in silicon peak intensity relative to the corresponding decrease in surface carbon. No change in the surface chemistry is apparent, nor is there a change in the Si:O ratio.

Insulating surfaces, such as a minerals or glasses, can be cleaned with an oxygen plasma, before charging electrostatically to the extent that low-energy ions are repelled. While the plasma itself must be electrically neutral, the impinging atoms, ions, and electrons incident on an insulating material may eject electrons, causing a sample to charge positively. The effect of surface charging can be seen as a ‘dark’ region in front of the surface of insulating samples, of initial width ~1 mm and expanding with exposure time. Charging, however, does not preclude the ability of the ions and atoms to clean an insulator surface effectively. An example of carbon removal from forsterite, a dielectric silicate mineral (Fig. 7), shows the effect of 30-s oxygen plasma exposure. The C is reduced to 10%, while the Mg Auger peaks and Si, Mg, and O photoelectron peaks all intensify. There is no increase of oxygen peaks intrinsic to the material, we determine the efficacy of the oxygen plasma produced by the constricted-anode source. All XPS spectra were acquired with a Physical Electronics Inc. 560 XPS/SAM instrument, equipped with a double-pass cylindrical mirror analyzer, dual-anode X-ray source, and a low-energy electron flood gun. XPS survey spectra were taken to assess relative elemental changes (spectrometer energy resolution: 3.2 eV); high resolution spectra were taken to quantify changes in surface chemistry (spectrometer energy resolution: 0.6 eV). The analysis chamber base pressure was maintained at ∼5 × 10⁻¹⁰ Torr with a combination 200 l/s ion pump and Ti sublimation pump. The plasma source was mounted in the introduction/preparation chamber, perpendicular to the sample transfer rod. Samples were mounted onto the transfer rod in the load lock chamber which was then evacuated with a turbo pump backed by a scroll pump. The sample could then be admitted directly to the analysis chamber. After taking initial XPS spectra, the sample was transferred back to the load lock chamber and exposed to the oxygen plasma for a period of time, usually less than 1 min. After exposure, the plasma source gas is turned down, quenching the plasma. After pumping the oxygen from the load chamber (<5 min), the sample was readmitted to the analysis chamber.

A copper sample with a thin gold deposit, 100 nm thick, was exposed to the oxygen plasma for varying times and analyzed before and after plasma treatment; the results are shown in Fig. 5. As exposure increases from 0 to 600 s, the atomic concentration of C decreases from 45 to 10%. Concurrent with the reduction of the carbon overlayer, there is an increase in the intrinsic Au and Cu peaks. However, the O : Au ratio does grow with increasing oxygen plasma exposure due to oxidation of copper. Continued plasma exposure beyond 5 min does not increase the surface oxygen further. Plasma etching allows minor constituents and impurities to be measured, rather than being attenuated or obscured by the surface hydrocarbons.

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Figure 4. Energy spectra for atomic and molecular oxygen. Ninety percent of the ions have energies smaller than 28 and 33 eV for O\(^+\) and O\(_2\)\(^+\), respectively.

Figure 5. Effect of O\(_2\) plasma from constricted-anode source on surface hydrocarbons as a function of exposure time. The treatment reduces the surface concentration of carbon from 44 to 10% (atomic percent). The intermediate values are 29, 15, and 11%. relative to forsterite’s other constituents – only the removal of surface hydrocarbons.

Discussion and Conclusions

While plasma cleaning is fairly novel within the field of surface physics, it has become a standard practice for sample preparation in electron microscopy.\(^{[12]}\) In this application it is observed that, in addition to cleaning the samples, argon/oxygen preprocessing also appears to reduce hydrocarbon buildup at the electron beam spot.\(^{[13–15]}\) These plasma cleaners typically utilize a radio frequency plasma in a cavity where the sample is inserted.\(^{[13,15]}\) The main drawback of the radio frequency (RF) plasma for surface analytical application is the high energy of the ions that can preferentially sputter some components of the sample thus changing its surface composition.

Another method uses ozone or a combination of ozone and ultraviolet (UV) radiation to remove hydrocarbons from samples in surface analytical instruments.\(^{[16,17]}\) These sources appear to work well, the ozone/UV source being most efficient, but are somewhat more complicated in nature (ozone generation) and require significantly longer exposure times (hours) compared to the seconds needed with our plasma source.

The constricted-anode plasma source can also operate with other gases, besides oxygen. Activated hydrogen, nitrogen, and other molecular compounds may also be useful as chemical...
cleaning or etching agents for various applications. We have tested this plasma source with air, which forms a white–blue plasma under similar conditions to the oxygen, and found that it removes hydrocarbons from surfaces but required longer exposure times. We plan future studies using the source with hydrogen, for the removal of both hydrocarbons and air-formed metal oxides.

In summary, we have expanded and tested the design of the constricted-anode plasma source and adapted it for in situ use on a surface analytical system. We find that oxygen plasma removes effectively and efficiently residual hydrocarbons and adventitious carbon from the surface of different types of materials. Measurements confirm that the source chemically etches surfaces with low-energy ions, radicals, and activated molecules, without altering the intrinsic surface stoichiometry of nonoxidizing materials.

Acknowledgements

This work was supported by the NASA LASER (Grant: NNX08AX11G) and Cosmochemistry (Grant: NNX08AG72G) programs.

References