(54) Title: PROCESSING DEVICE USING MULTICHARGED IONS

(57) Abstract: A material processing device that couples a spark discharge to a laser multicharged ion source to enhance the production of multicharged ions and increases ionization while simplifying structure. The processing device is capable of laser generation of multicharged ions for applications such as deposition and implantation. The ion beam of the device includes an electrostatic energy selector for controlling the energy of the ions used in processing. Some processing devices have the option to select ion charge over a wide range. The ability to select ions from a large spread of kinetic energy, and optionally with different charge states, offers a processing device with flexibility and applications in the areas of nanotechnology, microelectronics, and semiconductor processing.
PROCESSING DEVICE USING MULTICHARGED IONS

[0001] CROSS-REFERENCE TO RELATED APPLICATION

[0002] The present application claims the benefit of U.S. Provisional Patent Application No. 61/585,739, filed January 12, 2012, the entire disclosure of which is hereby incorporated by reference.

[0003] STATEMENT REGARDING GOVERNMENT SUPPORT

[0004] None.

[0005] FIELD OF THE INVENTION

[0006] This application relates generally to the field of nanotechnology processing, and more particularly to a device, system, and approach for a spark assisted laser source of multicharged ions, also known as multiply, heavily, or highly charged ions.

[0007] BACKGROUND

[0008] There is a need for more efficient, cost effective devices or systems for the fabrication of nanostructures. A number of nanotechnology processes are currently considered overly complicated to implement and expensive. These include, without intending to be exhaustive, conventional processes for the fabrication of semiconductor quantum dots, the fabrication of nanometer dielectric films, or the key process of ion implantation, which is useful in doping and surface treatments. Some of the challenging underlying steps for processing of nanotechnology materials are laser etching, cleaning, smoothing, adhesion enhancement, or preconditioning of semiconductor surfaces.

[0009] Multicharged ions (MCIs) have attracted significant attention for nanoprocessing and nonfabrication. The interaction of MCIs with solids differs significantly from that of singly charged ions. For singly charged ions at kinetic energies lower than $\sim$5 keV, the interaction is dominated by ion projectile-target nuclei interactions, which results in surface sputtering, intermixing, and defect generation. For MCI, with increased charge state the ions carry substantial potential energy, which is the sum of the ionization energies of the stripped electrons. The MCI interaction with the solid
involves the release of this potential energy in addition to the kinetic energy of the MCI. This potential energy can be significantly more than the MCIs’ kinetic energy. For example, for Ar$^{15+}$ the potential energy is $\sim 5$ keV, while for Xe$^{52+}$ the potential energy is $\sim 100$ keV. Upon interaction with a solid, this potential energy is released in electronic exchange interactions, inducing an electronic excitation of the solid. Moreover, unlike the ion kinetic energy, which is deposited over an extended track in the bulk, for sufficiently slow MCI, the release of potential energy can be localized to a depth of a few nanometers at the surface. That highly localized energy can be channelled into the generation of nanofeatures.

High current MCIs may be produced using electron cyclotron resonance ion sources (ECRIS), electron beam ion sources (EBIS), and laser multicharged ion sources (LMCI). While both ECRIS and EBIS sources operate well for continuous MCI production, they are generally considered to be costly machines. ECRIS and EBIS generate MCIs from gases; therefore, unless there is some way of introducing ions into them, they cannot be directly used for ion production from solids. One approach that may overcome this problem is the use of a laser to ionize material and to inject the ablated materials into the ECRIS or EBIS sources. In the past few years, there has been considerable interest in developing LMCI sources for particle accelerators, ion implantation, nonofabrication, and extreme ultraviolet source development for lithography. However, there are a few LMCI sources presently used for deposition and implantation. A modest laser energy of 0.5 mJ, 100 femtosecond Titanium:Sapphire (or fs Ti:sapphire) laser, focused to provide peak intensity of $3 \times 10^{16}$ W/cm$^2$, results in ion energies that depend on ion charge and extends up to $\sim 300$ keV for Si$^{10+}$. The ion current density per laser pulse measured by a microchannel plate located 60 cm away from the Si target was $10^5$ ion/cm$^2$, which corresponds to $\sim 10^8$ A/cm$^2$ at the plasma source. This ion yield per laser pulse, when operated at 1.5 kHz, is sufficient for many applications in implantation and deposition. However, cost has remained a challenge for these approaches.

In general, the high cost of these processes using conventional approaches has limited their wider application.
SUMMARY

Disclosed herein is a device using multicharged ions to process a material. This processing device includes a target vacuum chamber, a processing vacuum chamber, and a vacuum ion beam line. The target vacuum chamber may be configured to receive a target, the target vacuum chamber also defining a target vacuum chamber outlet. The processing vacuum chamber may be configured to receive the material for processing, with the processing vacuum chamber defining a processing vacuum chamber inlet. The vacuum ion beam line defines an interior ion track line or ion beam path with an ion beam inlet into the ion track line and an ion beam outlet from the ion track line. The vacuum ion beam line may generally be interposed between and in communication with the target vacuum chamber and the processing vacuum chamber with the ion beam inlet engaged with the target vacuum chamber so as to receive ions from the target vacuum chamber outlet and the ion beam outlet engaged with the processing vacuum chamber so as to discharge ions into the processing vacuum chamber inlet. Within the vacuum ion beam line is included an electrostatic energy selector. The target vacuum chamber, processing vacuum chamber, and vacuum ion beam line may be at ground potential during operation.

Embodiments of the processing device include a pulse laser system configured to emit a pulse of light at a first energy, the pulse laser system oriented such that the pulse of light is incident upon a point of the target positioned within the target vacuum chamber. A spark generator system is included, the spark generator system having a pulse generator circuit coupled to at least two electrodes, with the spark generator system configured to generate a spark at a second energy. The device includes a control system, or various interoperable control elements, the system being in operable communication with the pulse laser system, the spark generator system, and the electrostatic energy selector for controlling the emission of the pulse from the pulse laser system and the generation of the spark from the spark generator system.

In operation, the target vacuum chamber and the pulse laser are disposed in relation to each other such that the pulse incident upon the target generates a beam of a plurality of multicharged ions directed to the target vacuum chamber outlet and a plasma sheath proximate to the point of incidence on the target, and the pulse generator circuit and electrodes are disposed with respect to the target to generate a spark within
the plasma sheath. The target vacuum chamber, processing vacuum chamber, and vacuum ion beam line are configured such that when a vacuum is applied to the target vacuum chamber, processing vacuum chamber, and vacuum beam line, the plasma sheath produces a quasi-electrostatic field sufficient to accelerate the multicharged ions of the beam from the target vacuum chamber through the ion track line of the vacuum ion beam line to the processing vacuum chamber for processing the material without an external accelerating electromagnetic field. The control system triggers the pulse of the laser system and the spark of the generator system in such a manner so that the first and second energy contribute to a predetermined or desired on beam energy at the processing vacuum chamber. In this way, the device may process the material with multicharged ions. Some embodiments of the device may include a laser system has a laser pulse duration of about 100 femtoseconds or less.

[0016] Embodiments of the processing device may include an ion charge selector interposed between the vacuum ion beam line and the processing vacuum chamber, and in communication with the control system. The ion charge selector may be a semi-cylindrical analyzer followed by time-of-flight detector. The ion energy E and mass-to-charge ratio M/Z dependent on the voltage applied to the analyzer U according to the relations:

\[ kU = \frac{E}{Z} \text{ eV}, \]

\[ t = \frac{\sqrt{2m}}{\sqrt{Z}} \sqrt{\frac{k}{2U}} \text{ s}, \]

where \( t \) is the multicharged ion time-of-flight, and \( k \) is a constant dependant on the analyzer geometry. The ions may have an energy to charge ratio equal to the product of \( k \) and \( U \).

[0017] In some embodiments, the processing device target may be a solid laser ablation target. In some cases, the target and the electrodes may be fabricated of the same material. The electrodes may be fabricated of one of carbon or tantalum. Some versions of the device may include an extraction grid or Einzel lens disposed about the vacuum ion beam line for the focusing ions within the vacuum ion beam line.

[0018] In other embodiments, the pulse generator circuit may generate a pulse with a rise
time of about 5 nanoseconds to about 100 nanoseconds. The pulse generator circuit may generate a pulse with a duration of about 10 nanoseconds to about 1 microsecond, depending on the application. Some embodiments may benefit from a deceleration system having electrostatic lenses and filters, interposed between the beam line and the processing vacuum chamber for reducing kinetic energy of the multicharged ions.

[0019] BRIEF DESCRIPTION OF THE DRAWINGS

[0020] Figure 1 illustrates an embodiment of a target assembly for a Spark-Assisted Laser Multicharged Ion (SALMCI) source.

[0021] Figure 2 is a schematic of an embodiment of a target vacuum chamber and vacuum ion beam line for the processing device.

[0022] Figure 3 illustrates an embodiment of a processing vacuum chamber with in situ reflection high-energy electron diffraction gun.

[0023] DETAILED DESCRIPTION

[0024] A spark discharge may be coupled to a laser multicharged ion (MCI) source in order to significantly enhance the production of multicharged ions, increasing ionization while reducing cost. The development of an efficient LMCI deposition and implantation system or generically, processing device, with the ability to select ion charge over a wide range will enable new applications and research activities that depend on the MCI kinetic energy and charge selected, such as microelectronic development and biomedicine. The ability to select ions from a large spread of kinetic energy, and optionally with different charge states, gives a processing device with an LMCI source many applications in the areas of nanotechnology, microelectronics, and semiconductor processing.

[0025] An important subset of MCIs is that of ultraslow multicharged ions (USMCIs). USMCIs are ions with a kinetic energy per charge of only a few eV/q. They can interact with surfaces mainly through their potential energy, rather than their kinetic energy. Therefore, USMCIs are surface selective and can allow for low temperature processing given their large potential energy. A single USMCI approaching a
semiconductor surface creates an image charge on the semiconductor surface. This image charge accelerates the USMCI towards the surface in the interaction zone. As the USMCI approaches the surface (~1 nm), it extracts many electrons from the surface (~three times its initial charge). These electrons fill outer shell levels resulting in the formation of a “hollow atom or ion.” Ultrafast auto-ionization of the hollow ions yields highly charged ions that interact with the positive charge buildup at the semiconductor surface. The created repulsion force competes with the attraction force of the image state. The resulting slowdown of the MCI has been referred to as the “trampoline effect.” If the initial charge of the USMCI is high enough, the repulsive force will overcome the image charge attraction and the MCI can be reflected from the surface. An MCI with enough kinetic energy to overcome the repulsion force will strike the surface and transfer its potential energy. These MCIs can be used to grow thin films and quantum dots. In this noncontact interaction, the high potential energy of the ion can remove a large number of weakly bonded surface atoms, with little or no modification deeper than the top two monolayers. One USMCI can break the Si–H bond of a hydrogen-terminated Si surface over a few to a few tens of nanometer radiuses. When a reactive gas, such as O₂, is present in the processing vacuum chamber, oxides can be formed over these selected surface areas resulting in oxide nanodots.

[0026] Applications of USMCI, which may be generated from a processing device with the present LMCI by selection of slow ions followed by ion deceleration, include nanoscale surface modification, nanofabrication, and MCI reflection lithography. Precise etching, cleaning, smoothing, adhesion enhancement, or preconditioning of semiconductor surfaces on an atomic scale in ultrahigh vacuum (or UHV) using USMCI have been demonstrated. The results show the ability of MCIs to pattern SiO₂ and to produce nanodots on Si surfaces. The fabrication of nanometric-thickness films of oxides, nitrides and oxynitrides on semiconductors, as well as fabrication of nanolayers and quantum dots on semiconductors are also possible.

[0027] As noted above, high current MCIs have been produced using ECRIS and EBIS, and certain LMCI, but these approaches have proven problematic.

[0028] In contrast, a spark-assisted laser multicharged ion source (SALMCI) may be driven with a 2.4 mJ, 80 fs Ti:sapphire laser operating at 1.5 kHz. In addition to the higher
laser energy available for use, the coupling of the laser plasma to spark discharge amplifies the MCI generated. The spark-assisted LMCI source also offers a significant cost reduction and simplified design compared to ECRIS and EBIS sources. The SALMCI avoids the use of an ion acceleration stage since the ions generated from the laser plasma are accelerated by a quasi-electrostatic field produced in the plasma sheath or plume. This plasma sheath or plume is dependent on the plasma temperature, producing a relatively well-collimated ion beam perpendicular to the target surface. The LMCI source may be used within a processing device that involves a target assembly of MCIs and a target vacuum chamber, a vacuum ion beam line; and a processing vacuum chamber. Figures 1 - 3 are provided for general reference throughout the detailed description.

[0029] Figure 1 is a schematic that illustrates an aspect of the configuration of some elements of an embodiment of processing device 10. This schematic shows portions of target assembly 30 for a SALMCI source, with laser system 20 as a Ti:sapphire fs laser (which may be used, for example, with an intensity of $10^{16}$-$10^{17}$ W/cm²) emitting a pulse of light at a first energy incident on a target 33 to generate ions. A spark generator system 45 is shown as a circuit in which a spark at a second energy is pulsed across at least two coupled electrodes 40; this example is shown as a Blumlein line pulse generator circuit, with power supply 45a, resistor 45b, and capacitor 45c. Control elements or system (discussed below) are in operable communication with the pulse laser 20 and the spark generator system 45 for controlling the emission of the pulse and the generation of the spark. Ion beam 50 may pass through optional extraction grids 80 and Einzel lens 60.

[0030] Figure 2 is an illustration of the configuration of additional elements of an embodiment of processing device 10. This illustration shows target vacuum chamber 100 of target assembly 30, and vacuum ion beam line 200 to the point at which ion beam 50 branches off for processing vacuum chamber 300. This illustration shows other aspects of target assembly 30, such as target vacuum chamber outlet 175, one or more viewports 106, heating wire 102, XYZ manipulator 103, thermocouple 104, and Ar+ gun 108. In this example, a target vacuum chamber 100 and vacuum ion beam line 200 in which a semi-cylindrical analyzer selects ions with certain mass/charge and pulsed deflection plates are then used to select charge. Electrostatic energy selector 55
may be used for analyzing and selecting energy of ion beam 50. Laser 20, shown with aspects of a control system including pin diode 22, variable delay device 24, and high voltage pulser 26, emit pulses incident on target 33, generating ions and plasma sheath or plume 110. Other elements, such as computer processors, non-transitory memory, communication networks, etc., may be included within such a control system. MCI's form ion beam 50 and exit target vacuum chamber 100 at target vacuum chamber outlet 175, at which point ion beam 50 passes via vacuum ion beam line inlet 225 or aperture into vacuum ion beam line 200. Ion beam 50 may pass via vacuum ion beam line 200, past electrostatic energy selector 55, through Einzel lens 60, and ion charge selector 70; at that point, ion beam 50 may be directed to processing vacuum chamber 300 (not shown). In this figure are also shown Faraday cup 85, micro-channel plate 230, charge coupled device (CCD) detector 362, and computer 364. In this way, the target vacuum chamber 100 and the pulse laser 20 are disposed in relation to each other such that the pulse incident upon the target 33 generates a beam of a plurality of multicharged ions directed to the target vacuum chamber outlet 175 and a plasma sheath or plume 110 proximate to the point of incidence on the target 33, and the pulse generator system and electrodes 40 are disposed with respect to the target 33 to generate a spark within the plasma sheath 110. The control system triggers the pulse of the laser system 20 and the spark of the spark generator system 45 (not shown) such that the first and second energy contribute to a predetermined or desired energy for ion beam 50.

[0031] As discussed below, the target vacuum chamber 100, processing vacuum chamber 300, and vacuum ion beam line 200 are at substantially ground potential, and are configured such that the plasma sheath produces a quasi-electrostatic field sufficient to accelerate the multicharged ions of the beam 50 from the target vacuum chamber 100 through the ion track line of the vacuum ion beam line 200 to the processing vacuum chamber 300 for processing the material 15 without an external accelerating electromagnetic field.

[0032] Figure 3 illustrates elements of processing device 10, including processing vacuum chamber 300. Processing vacuum chamber 300 receives ion beam 50 as it exits beam line 200 via beam line outlet 275 and processing vacuum chamber inlet 325. Processing vacuum chamber 300 may include optional reflection high-energy electron
diffraction (RHEED) gun 340 in situ, in which a deceleration stage allows for generation of USMCIs. In this figure are also shown decelerator or deceleration system 90 and electrostatic steering device 95 as ion beam 50 enters processing vacuum chamber 300. Processing vacuum chamber 300 may also include one or more thermal cracker sources 370, residual gas analyzers (or RGA) 380, viewports 306, microchannel plates 230, phosphor screens 330, CCD detectors 362, and computers 364 associated with such detectors. Ion beam 50 may then be incident on a substrate 16 of material 15.

[0033] The coupling of energy from a spark discharge to laser plasma enhances the signal from laser-induced breakdown spectroscopy (LIBS). For example, electrodes 40 for spark discharges may be placed ~2 mm above the surface of the LIBS target 33 and the laser plasma may then be used to trigger a spark. A 40-ns pulse from a Nd:YAG laser 20 (with a very weak intensity of 10^8 W/cm^2) has been used in testing. There was also no attempt in the test to tailor the spark discharge pulse or reduce its pulse width since the objective in that case was to increase the integrated LIBS signal, which is increased by an increase in plasma density, temperature, and the length of time the plasma is sustained. For LMCI generation, an amplified femtosecond Ti:sapphire laser with power density of 10^{16}-10^{17} W/cm^3 (8-9 orders of magnitude more than in the LIBS experiment) could be used. Optional extraction grids 80 and Einzel lens 60 may be used for better focusing of the ion beam 50 within the vacuum ion beam line 200. Because of the high acceleration of the ions in the sheath or plume 110 of the laser plasma and the directionality of the ions generated, the extraction grids 80 and Einzel lens 60 may not be necessary for many applications. In order to maximize the spark discharge power, a fast Blumlein line pulse generator may be used. The electrodes 40 for the spark discharge may be placed a few millimeters on top of the surface of target 33, so that the spark can deposit its energy in the laser plasma (See, e.g., Figure 1). For metallic MCIs, the target 33 and the spark discharge electrodes 40 may be made, when practically possible, out of the same metal in order to minimize introduction of another element in the plasma by electrode sputtering. Otherwise, and for nonmetallic ions, the spark discharge electrodes 40 may be made out of a low sputter yield material, such as carbon or tantalum, even though electrode sputtering should not be much of a concern since the MCIs are selected in the ion beam transport line 200.
For MCI generation of gases such as O₂, Xe, or Kr, a liquid nitrogen cooled finger (not shown) could be used to form a solid layer of these gases, which can then be ablated. Alternatively, the femtosecond laser 20 may be used to directly breakdown the gas by focusing it tightly, causing dielectric breakdown. Laser breakdown of NH₃ has been previously used to grow InN, for example.

In many applications, the material of the target 33 will be a solid. The spark discharge will be generated in an UHV over distances or gaps of a few millimeters. Under these conditions, the plasma channel that constitutes the spark will be generated from the material of the laser ablation target 33. Vacuum breakdown is initiated by electrons emitted from the cathode. If the associated currents are high enough, the electrode material could be evaporated, ionized and forms a highly conductive plasma channel. The materials for the laser target 33 and the spark electrodes 40 can be the same.

To generate dense plasma with the spark discharge, breakdown may be instigated as fast as possible to deposit energy in the spark faster than it can dissipate in recombination. This may be achieved by applying high voltage pulses with fast rise-times from pulse generators with small source impedance, close to the impedance of the spark discharge. Rise times of 5-100 nanoseconds are contemplated as applicable to various embodiments. Although different approaches may support the proposed MCI source for processing device 10, such as capacitive discharge and Marx bank circuit, the use of a Blumlein line setup allows the provision of rectangular voltage pulses with rise times of a few to several tens of nanoseconds. Pulse amplitude and duration can be controlled and the spark can be synchronized easily with the laser pulse. Depending on the pulse duration, it will be possible to achieve breakdown with pulses of ~100 ns. However, pulse duration of about 10 ns to about 1 microsecond are expected for various applications. A fast initiation of the spark is enabled by the short rise time of the pulse, which will keep time lags short and drive fast current rise times once a conductive channel has been established. The lifetime of the spark is dependent on the energy that is provided from the pulse generator during breakdown. To provide the energy fast to the spark during breakdown, a Blumlein pulse generator may be configured as fast cable discharge, using several cables in parallel to minimize the impedance of the system, or a low inductance pulse forming line built from fast components. An additional advantage of the Blumlein line concept is that before
breakdown, a voltage twice as high as the charging voltage may be applied to the gap.
If higher voltages are required, the concept can further be expanded into a stacked
Blumlein line, which can multiply the input voltage by the number of stages, without
the disadvantage of a slow rise time known for a Marx bank.

[0037] The target 33 may be cleaned by direct heating (i.e., for Si and Ge) or by Ar+ bombardment in UHV. The spark discharge may be designed to allow for their positioning off the surface for Ar+ cleaning. Cleaning the target 33 results in far more efficient production of MCIs.

[0038] The vacuum ion beam line 200 connects the target vacuum chamber 100 with the process chamber 300 and is used to transport the ions from the source or target assembly 30 to the sample of material 15 in the processing vacuum chamber 300, and to select ion kinetic energy and charge, as shown in Figure 2. A beam with a homogeneous content of ions of a desired species and ionization state is generally very much desired in such a processing device 10. Since ions extracted from the source have different ionization states and could be of different elements, it is important to select the right ions. Ion selection based on mass and charge from the mix of ions produced, which normally contains a rapidly diminishing quantity of higher charged ions, is usually achieved by mass/charge spectrometry of the beam with a strong magnet, which is costly; however, a lower cost electrostatic ion selection is preferable. The ions produced by such a laser source have very high energy (up to \(-150\) kV and when including the energy tail even to \(-350\) kV) and high charge states (up to \(+50\)). For ion selector 70, a semi-cylindrical analyzer followed by a time-of-flight detector (not shown) may be used. The ion energy \(E\) and mass-to-charge ratio \(M/Z\) are dependent on the voltage applied to the analyzer \(U\) according to the relations:

\[
kU = \frac{e}{z} \quad \text{eV}, \quad (1)
\]

\[
t = e \sqrt{M} \sqrt{\frac{k}{2u}} \quad \text{s}, \quad (2)
\]

where \(t\) is the ion time-of-flight, and \(k\) is a constant that depends on the geometry of the analyzer. Ion selector 70 is disposed prior to processing vacuum chamber 300, and may be interposed within portions of a modular beam line 200 or between beam line
200 and processing vacuum chamber 300. For certain applications, such as surface cleaning or etching, an ion beam 50 consisting of a combination of MCIs of different charges, may be acceptable. This would allow the elimination of the selector 70. A modular design of the beam line 200 would make this possible, by permitting removal of the energy selector 70 flange and repositioning of processing vacuum chamber 300.

[0039] The homogeneity of a beam (intensity distribution) can vary over its cross-section, which is expected to be elliptical in shape with major and minor axes of several centimeters. The uniformity of the ion beam 50 at the material 15 depends on the construction of the vacuum ion beam line 200. One method commonly used to improve ion beam uniformity is the use of diaphragms or jaw slits to eliminate all but the central ions close to the beam axis. This not only reduces the density of the ions on the target 33, but also causes problems associated with heating of the diaphragm, i.e., gas desorption and contamination of the ion beam and the system by sputtered of the diaphragm. The pulsed operation of the LMCI source for processing device 10 reduces this ion-loading effect, compared to ECRIS and EBIS. Electrostatic X-Y steering (or guiding) device 95 will help guide the beam. Electrostatic steering devices 95 are preferable to magnetic devices because of their compact size and low cost. However, for very high ion energies the required steering voltage might be high.

[0040] Many applications require deceleration of the MCIs. For surface processing, an advantage of processing device 10 is the ability to deliver potential energy, with reduced or no damage to the surface or substrate 16 of the material 15 by high kinetic energy ions. In deceleration of the MCI beam directed perpendicularly to the substrate 16 of the material 15, one needs to consider the energy dispersion of ions extracted from the source and additional energy dispersion caused by non-uniformity of the decelerating electric field. These can be minimized by optimizing the construction of the deceleration system 90 using electrostatic lenses and filters and by stabilization of the deceleration conditions. The high voltage power supplies for the steering device 95 and the deceleration system 90 stages preferably are very stable, unlike those in general purpose low-stability instruments. The generation of high ion charges and the capability of decelerating them to very low kinetic energies is a new and important advantage of processing device 10. An LMCI without ion selection and deceleration would not be useful for low kinetic energy surface treatment.
A Faraday cup 85 may be used to measure the ion current. It may be advantageous to use two or more Faraday cups 85 at both ends of the beam line 200 to monitor ion transport loss.

In ECRIS the ion source is usually kept at a high potential of about 10-30 kV. The vacuum ion beam line, which may be several meters long, is usually maintained at ground potential. The line is under UHV to prevent the ions from interacting with residual gas and losing their charge. To reduce the ion transit time and the probability of deionization, the ions need to be transported at high velocities, requiring an accelerating potential of an order of 10 kV at the beginning of the line and a controlled potential to decelerate the ions to the desired energy before interaction with the sample. An aspect or advantage of the LMCI processing device 10 is that the source or target assembly 30 may be kept at ground potential, because the ions accelerate in the plasma sheath to energies dependent on the laser and the spark discharge parameters. Beam line 200 may be at a consistent ground potential.

The vacuum ion beam line 200 may be kept under UHV with a vacuum system. Such a vacuum system may include ion pumps or oil-free turbomolecular pumps. Solenoid valves at both ends of the beam line 200 may isolate the beam line 200 under UHV for maintenance of the target and processing vacuum chambers 100, 300.

The Einzel lens 60 disposed after the electrostatic energy selector 55 may control the size of the ion beam 50 delivered to the processing vacuum chamber 300. The energy/charge ratio (E/Z) of the ions passing the electrostatic energy selector 55 may be obtained from Equation (1). For each voltage U, ions with different charges will pass the energy selector 55. The higher the charge of the ions for an element, the more kinetic energy it will have. Therefore, it is possible to use time-of-flight detection to analyze the charge distribution of these ions. Also, by applying a pulsed voltage to a pair of deflection plates, it is possible to select certain ion charge. A PIN diode 22, that detects a reflection from the femtosecond laser 20, generates a pulse that is used to trigger a high voltage pulse generator after being delayed in an electronic variable delay generator 24. The ion beam 50 is passed through deflection plates and is collected on a movable Faraday cup 85 to measure total current. To observe the MCI beam profile, the Faraday cup 85 may be withdrawn and the ion beam 50 allowed to be incident on a set of microchannel plates (MCP) 230 that are proximity focused to a
phosphor screen 330. By timing the high voltage pulse on the deflection plates to select ions with a certain charge, it is possible to deflect ions with a particular charge into the processing vacuum chamber 300.

[0045] The processing vacuum chamber 300 may be operated at UHV and will contain the material 15 or sample to be exposed to the MCI ion beam 50 and surface diagnostics tools, as shown in Figure 3. In one embodiment, two UHV systems with surface analysis tools (not shown) were used integrated with the MCI. The modular design of the SALMCI processing device 10 allowed for it to be used in different deposition chambers. The selected MCI with certain E/Z and M/Z ratios could be decelerated to produce USMCI. The X-Y electrostatic steering devices 95 were used to position the MCI on the sample of material 15. A sample was then mounted on an X-Y-Z stage with axial and azimuthal rotation. If the substrate 16 of material 15 were moved out of the MCI ion beam 50 path, the ion beam 50 would hit an MCP 230 detector (not shown) that imaged the charge to check the MCI beam profile. Alternatively, the ion intensity distribution on a Si substrate could be monitored using one or more intensified CCD camera 362 to monitor florescence from the surface of the substrate. The processing vacuum chamber 300 may contain a RHEED gun 340 capable of monitoring less than 0.05 ML growth and an Auger spectrometer (not shown) may be attached to the chamber for in situ chemical analysis.

[0046] Including a laser-beam splitting device (not shown) or beam switching capability to the system and rapidly switching the ion beam 50 or directing a portion to the processed substrate 16 permits simultaneous generation of MCI's and laser-assisted surface processing.

[0047] The SALMCI source processing device 10 may be connected to an UHV scanning tunnelling microscope (STM) integrated with a pulsed laser deposition (PLD) chamber (not shown). This would allow for exposing a sample to MCI and then moving it under UHV to the STM chamber. The sample could then be grabbed with a manipulation tool or wobble stick and probed. The system can probe, with atomic resolution, the surface structure after MCI exposure. Moreover, embodiments of this processing device 10 have the ability to expose a clean thin film fabricated by PLD or Molecular Beam Epitaxy (MBE) to MCI. This capability is particularly valuable in semiconductor fabrication as it gives the ability to perform ion implantation, shallow
implantation, strain engineering, surface texturing, and nanometric quantum dot deposition in conjunction with PLD or MBE, and to study the growth by STM without breaking UHV.

[0048] ADDITIONAL EMBODIMENTS

[0049] A spark-assisted laser multicharged ion (SALMCI) source processing device 10 would result in a significantly higher charge state out of practically any solid target than is possible with present LMCI sources driven with a high-repetition rate (1.5 kHz) femtosecond Ti:sapphire laser. The spark-assisted LMCI source processing device 10 also offers a significant cost reduction and simplified design compared to MCI sources based on electron cyclotron resonance ion sources (ECRIS) and electron beam ion sources (EBIS). An aspect of embodiments of processing device 10 is to amplify significantly the energy contained in the laser-produced plasma by coupling the laser-produced plasma with a spark discharge. Therefore, while a laser energy pulse of ~1 mJ is used in the LMCI production, the energy deposited by the spark discharge can be ~1 J or more, resulting in three-orders-of-magnitude increase in energy deposition. Also, by proper pulsed power circuit design, the spark discharge can be used to deposit this energy in tens of nanoseconds, resulting in significant enhancement of MCI production. The enhancement of LMCI production by the spark discharge also can be used for MCI production from gases, such as noble gases, since the focused femtosecond laser can cause dielectric breakdown in the gases. The proposed LMCI processing device 10 also avoids the use of an ion acceleration stage, since the ions generated from the laser plasma are accelerated by the quasi-electrostatic field in the plasma sheath, producing a relatively well-collimated ion beam perpendicular to the surface of target 33, which for a modest laser energy of 0.5 mJ for 100 fs Ti:sapphire laser 20 can result in ion energies that depend on ion charge and extend up to ~300 keV for Si^{10+}. Moreover, the pulsed nature of the produced MCIs facilitates charge state measurement by time-of-flight technique and selection by gated deflection plates. In addition, the pulsed nature of the LMCI source is ideal for time-resolved studies of ion surface interactions, and opens many possibilities to probe the mechanism of MCI-surface interaction through probing the temporal development of secondary electron emission and photo-luminescence. Generation of highly charged ions with well-identified kinetic and potential energies will enable
new research possibilities.

[0050] Processing device 10 may be used, for example, in the fabrication of nanometer dielectric films and nanostructures. Ultra-thin metal oxide high-dielectric constant films, such as hafnium oxides and oxinitrides may be fabricated by atomic layer deposition; however, this has several disadvantages, including contamination with precursors (the more important), filling of pores due to precursor penetration into porous dielectric, high process temperature, and low throughput. Use of an MCI approach mitigates those disadvantages. Silicon oxide and oxinitride films of excellent uniformity and quality have been fabricated with highly decelerated O$^{5+}$ beams (1 eV/charge).

[0051] Higher dielectric constant oxides, which are crucial to the future generations of nanodevices, were not previously fabricated by MCI approaches. The proposed spark-assisted LMCI source of processing device 10 will allow the deposition of Ta, Ti, and Hf nanometer thick oxides. In this case, the metal MCI beams will bombard the surface or substrate 16 of material 15 in the presence of a residual O$_2$ atmosphere in the fabrication or processing vacuum chamber 300. The expected availability of high ion charges, generated by SALMCI, will allow one to determine to what degree the kinetic bombardment of the surface or the electrostatic ion charge contribute to damage generated on the surface of material 15. The reduction of surface damage by the use of MCIs is important in device technology. The MCI approach of processing device 10 allows the removal of low-quality native oxides and other contamination from the surface of materials 15, such as semiconductors.

[0052] The high charge of MCI in processing device 10 can allow them to be channelled into pinholes and grain boundaries of the oxides, and fill in defects. Combining the two processes of MCI cleaning and MCI oxide formation will lead to development new fabrication process superior to the existing ones used in nanodevices and nanostructures. Previous work on crystalline nanodots on silicon may be expanded with the aim of improving the control of dimensions, size distribution and uniformity, and to fabricate multilayer nanodots with different oxide materials.

[0053] Processing device 10 may also be used in the fabrication of semiconductor quantum dots and various nanotechnology devices.
The use of ultraslow multicharged ions (USMCI) for QD growth with processing device 10 is attractive because USMCI cause minimal damage to the surface or substrate 16 of material 15 and the high charge results in significant electronic excitation. Surface excitation enhances epitaxial growth. With USMCI, epitaxially grown Ge/Si QDs may be fabricated at room temperature. One important issue is the control of Ge/Si ratio in the QDs. Because LMCI offers independent selection of MCI kinetic and potential energy, increased control on the Ge/Si mixing ratio and QD size and size distribution may be achieved. This ability may be particularly important when the optical properties of the quantum dots are to be controlled for applications in near IR detectors.

Nitride QDs have also been fabricated by PLD, and the use of USMCI will significantly improve size and size distribution control.

An alternative approach may be to use processing device 10 with heavy MCIs, such as Xe$^{4+}$, to cause craters or pits in the Si wafer surface that could also be utilized to synthesize QDs. These minute craters possess additional unsaturated Si covalent bonds (dangling bonds), which would render these sites the preferred location where Ge and other materials would attach to form confined QDs with superior dimensional control.

Processing device 10 may be used for the implantation of MCIs in semiconductors. Ion implantation is one of the key processes in modern microelectronic fabrication. This process utilizes singly charged ions, with energies typically from 0.2 keV (for shallow junction implantation) to ~2 MeV (for multiple-well doping). The kinetic projectile energy is of great importance. MCIs offer the possibility of using much lower kinetic energies during ion implantation, in particular, for ultra shallow implantation which is needed for nanodevices.

Processing device 10 may also be used for the implantation of highly charged high kinetic energy ions. High charge state ions require much less voltage for acceleration than single charged ions. If a voltage of 2 MV is used to accelerate single charge ions (q = +1), then for q = +50 to be accelerated to the same kinetic energy, it requires 50 times lower voltage (40 kV). Since most of the LMCIs are generated with a kinetic energy <10 keV, a relatively simple acceleration stage may be added in the ion beam
transport line 200 to accelerate these MCIIs to the 2 MeV kinetic energy. High-energy ion implantation of boron and aluminum into n-type silicon may be used to fabricate deep p-n junctions of mesa and planar type.

[0059] Another application of processing device 10 with MCIIs is in doping high-k transition metal oxides thin films. Doping can be used to modulate the band gap of oxides, such as TiO₂, by doping it with N or Co with less implantation damage than that caused with singly charged ions. Un-doped TiO₂ absorbs in the UV region and exhibits a strong photocatalytic effect upon irradiation with UV light. However, doping ultrathin TiO₂ films shifts the absorption into the visible wavelength region and activates the photocatalytic effect upon irradiation with visible light. This offers distinct advantages in various applications for TiO₂.

[0060] Processing device 10 may be used in the shallow implantation of slow highly charged ions. Fabricating very shallow (10-200 nm depth) ion-implanted junctions remains a problem in nanomanufacturing. Low-energy ion implantation in the range of 1 keV to 0.25 keV is typically used; however, at such low energies the implanted ions cannot be totally retained due to surface sputtering and backscattering. The use of molecules or clusters has been shown to enhance the productivity of the low energy ion implantation processes. By operating at higher energies, beam loss effects in ultralow-energy ion implantation are minimized. The use of B₁₈H₂₂ for shallow implantation of boron ions allowed the implanter to be operated at 20x the process energy. For example, a 500 eV B⁺ process may be achieved by operation at 10 keV. Slow MCIIs cause little damage on the surface and can be a good candidate to fabricate very shallow junctions. In addition, the LMCI source is capable of producing MCIIs of practically any element. The approach of using a compound can complicate the implantation process by introducing other elements. A potential device application is in fabricating shallow junctions for MOS field effect transistors.

[0061] Processing device 10 using a SALMCI source capable of producing highly charged ions would provide a valuable tool for many different fields. The approach of enhancing MCI production from laser plasma by combining it with a spark discharge has significant potential for cost and size reduction of the MCI source. The cost constraints on commercial MCI sources have so far been a factor limiting their wide applications. The widest area of applications that the proposed MCI source may find
is in the micro/nano-electronics area. Applications of processing device 10 may include development of new devices, quantum dot sensors (chemical, biological, and IR to UV detectors), and advanced solar cells. Other areas include development of highly sensitive methods of chemical analysis based on time-of-flight secondary ion mass spectrometry (TOF-SIMS) using MCI and many applications in biomedicine ranging from generation of monoenergetic x-rays for diagnostic imaging and cancer therapy to the generation of highly charged carbon ions for cancer therapy.

[0062] This design is an enabling technology for diverse fields from defense related applications (e.g. rail guns), sustainable energy (e.g. fusion reactors), environmental applications (e.g. water treatment) to medical applications (e.g. new tumor therapies). There should be few if any fundamental barriers to the acceptance of the technology by the manufacturing industry, once industrial scale systems are constructed.

[0063] Processing device 10 with SALMCI will offer high intensities of highly-charged ions at a much reduced cost compared to the ECRIS or EBIS systems and will make many existing pulse laser deposition systems convertible to efficient MCI systems with the addition of relatively low cost components. By allowing simultaneous generation of multicharged ions and laser-assisted surface processing, which is not possible with existing ECR or EBIT sources unless an additional laser is incorporated into the system, processing device 10 will open new technological possibilities at a low incremental price.

[0064] It is to be understood that the disclosed device, system, and approach are not to be limited to the exact configuration as illustrated and described herein. Accordingly, all expedient modifications readily attainable by one of ordinary skill in the art from the disclosure set forth herein, or by routine experimentation therefrom, are deemed to be within the spirit and scope of the disclosure.
IN THE CLAIMS

We claim:

1. A device using multicharged ions to process a material, the processing device comprising:
   a target vacuum chamber configured to receive a target, the target vacuum chamber defining a target vacuum chamber outlet;
   a processing vacuum chamber configured to receive the material for processing, the processing vacuum chamber defining a processing vacuum chamber inlet;
   a vacuum ion beam line defining an interior ion track line with an ion beam inlet into the ion track line and an ion beam outlet from the ion track line, the vacuum ion beam line interposed between and in communication with the target vacuum chamber and the processing vacuum chamber with the ion beam inlet engaged with the target vacuum chamber so as to receive ions from the target vacuum chamber outlet and the ion beam outlet engaged with the processing vacuum chamber so as to discharge ions into the processing vacuum chamber inlet, the vacuum ion beam line including an electrostatic energy selector;
   a pulse laser system configured to emit a pulse of light at a first energy, the pulse laser system oriented such that the pulse of light is incident upon a point of the target positioned within the target vacuum chamber;
   a spark generator system having a pulse generator circuit coupled to at least two electrodes, the spark generator system configured to generate a spark at a second energy;
   a control system in operable communication with the pulse laser system, the spark generator system, and the electrostatic energy selector for controlling the emission of the pulse from the pulse laser system and the generation of the spark from the spark generator system;
   the target vacuum chamber and the pulse laser disposed in relation to each other such that the pulse incident upon the target generates a beam of a plurality of multicharged ions directed to the target vacuum chamber outlet and a plasma sheath proximate to the point of incidence on the target, and the pulse generator circuit and electrodes are disposed with
respect to the target to generate a spark within the plasma sheath;

wherein the target vacuum chamber, processing vacuum chamber, and vacuum ion beam line are configured such that when a vacuum is applied to the target vacuum chamber, processing vacuum chamber, and vacuum beam line, the plasma sheath produces a quasi-electrostatic field sufficient to accelerate the multicharged ions of the beam from the target vacuum chamber through the ion track line of the vacuum ion beam line to the processing vacuum chamber for processing the material without an external accelerating electromagnetic field; and

wherein the control system triggers the pulse of the laser system and the spark of the generator system such that the first and second energy contribute to a predetermined ion beam energy at the processing vacuum chamber.

2. The processing device of claim 1, wherein the laser system has a laser pulse duration of about 100 femtoseconds or less.

3. The processing device of claim 1, further comprising an ion charge selector interposed between the vacuum ion beam line and the processing vacuum chamber, and in communication with the control system.

4. The processing device of claim 1, further comprising an ion charge selector interposed between the vacuum ion beam line and the processing vacuum chamber, wherein the ion charge selector is a semi-cylindrical analyzer followed by time-of-flight detector, and is in communication with the control system.

5. The processing device of claim 1, further comprising an ion charge selector interposed between the vacuum ion beam line and the processing vacuum chamber, wherein the ion charge selector is a semi-cylindrical analyzer followed by time-of-flight detector, is in communication with the control system, such that the ion energy $E$ and mass-to-charge ratio $M/Z$ dependent on the voltage applied to the analyzer $U$ according to the relations:

$$kU = \frac{E}{z} \quad \text{eV},$$

$$t = \frac{M}{z \sqrt{2U}} \quad \text{s},$$
where \( t \) is the multicharged ion time-of-flight, and \( k \) is a constant dependant on the analyzer geometry.

6. The processing device of claim 1, wherein the target is a solid laser ablation target.

7. The processing device of claim 1, wherein the target and the electrodes are fabricated of the same material.

8. The processing device of claim 1, further comprising one of an extraction grid or einzel lens disposed about the vacuum ion beam line for the focusing ions within the vacuum ion beam line.

9. The processing device of claim 1, wherein the electrodes are fabricated of one of carbon or tantalum.

10. The processing device of claim 1, wherein the pulse generator circuit generates a pulse with a rise time of about 5 nanoseconds to about 100 nanoseconds.

11. The processing device of claim 1, wherein the pulse generator circuit generates a pulse with a duration of about 10 nanoseconds to about 1 microsecond.

12. The processing device of claim 1, further comprising a deceleration system having electrostatic lenses and filters, interposed between the beam line and the processing vacuum chamber for reducing kinetic energy of the multicharged ions.

13. The processing device of claim 1, wherein the ions have an energy to charge ratio equal to the product of \( k \) and \( U \).

14. The processing device of claim 1, wherein the target vacuum chamber, processing vacuum chamber, and vacuum ion beam line are at ground potential.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
   IPC(8) - H01J 47/00, H01S 3/0977, H01T 23/00 (2013.01)
   According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
   Minimum documentation searched (classification system followed by classification symbols)
   IPC(8)-H01J 47/00, H01S 3/0977, H01T 23/00 (2013.01);
   Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
   Patents and NPL (classification, keyword; search terms below)

   Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
   PubWest, PatBase (USPTO, EPO, JPO, WIPO, PCT), GoogleScholar (PL, NPL), FreePatentsOnline (USPTO, EPO, JPO, WIPO, NPL);
   search terms: ion, laser, beam, multicharge, polenergized, pulse, spark, ignition, extract, grid, einzel, lens, ablate, time, flight, mass,
   charge, accelerate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tbody>
<tr>
<td>Y</td>
<td>US 2006/0145088 A1 (MA) 06 July 2006 (06.07.2006), Figs. 34, 41; para [0114]-[0121], [0127], [0155], [0160], [0194], [0198], [0201]</td>
<td>1-14</td>
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<tr>
<td>Y</td>
<td>US 4,709,373 A (SCOTT et al.) 24 November 1987 (24.11.1987), Fig. 1; col 1, In 39-52; col 3, In 23-67; col 4, In 15-35</td>
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<td>Y</td>
<td>US 4,498,183 A (LEVATTER) 05 February 1985 (05.02.1985), col 8, In 60-67; col 10, In 45-68</td>
<td>7, 9</td>
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☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
   "A" document defining the general state of the art which is not considered to be of particular relevance
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   "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

Date of the actual completion of the international search
06 April 2013 (06.04.2013)

Date of mailing of the international search report
26 APR 2013

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