IPDS's copy!
980 2939-0

LAYERED RESIST SYSTEM USING TUNABLE AMORPHOUS CARBON FILM AS A BOTTOM LAYER AND METHODS OF FABRICATION THEREOF

FIELD OF THE INVENTION

The present invention is directed to structures useful for fabricating integrated circuits (IC), in particular structures having a plurality of layers, more particularly having tunable thick bottom layer coatings based on amorphous carbon films to be used in a bilayer resist system and methods of fabrication thereof useful for fabricating.

BACKGROUND OF THE INVENTION

As device dimensions shrink to 0.25 μm and below for logic and memory chips the single-layer resists currently in use will not work with conventional exposure tools. Substrate reflections at ultraviolet (UV) and deep ultraviolet (DUV) wavelengths are notorious to produce standing wave effects and resist notching which severely limit critical dimensions (CD) tolerances. Notching results from substrate topography and nonuniform substrate reflectivity which causes local variations in exposure energy on the resist. Standing waves are thin film interference (TFI) or periodic variations of light intensity through the resist thickness. These light variations are introduced because planarization of the resist presents different thickness through the underlying topography. Thin film interference plays a dominant role in CD control of single layer photoresist processes, causing large changes in the effective exposure dose due to a tiny change in optical phase.

Linewidth control is one of the most important requirements for a useful microlithographic process. A typical criterion is that the printed linewidth must be within 10% of the target value. There are many process variables which can cause changes in linewidth. Figure 12 shows a simulation of how the resist linewidth varies with exposure energy. An exposure energy of roughly 10mJ/cm^2 prints a line which is quite close to the target dimension of 0.25 microns. An underexposed condition at 8.5mJ/cm^2 would print a .4 micron line and an overexposed condition at 12.5mJ/cm^2 would print a 0.14 micron line. The only way to print the desired 0.25 micron line to within the +-10% criterion is to carefully control the exposure energy.

Unfortunately, there are many process factors which can affect the exposure energy within the photoresist. The most important source of such exposure variation is due to thin film interference effects, as described in "Optimization of optical properties of resist processes" (T. Brunner, SPIE Proceedings Vol. 1466, p. 297, 1991). The thin films used in semiconductor fabrication, e.g. silicon nitride or silicon oxide, always have some variation in their thickness which leads to variation in the exposure energy going into the resist. Let us consider how things change when the photoresist is on top of a variable thickness of silicon oxide, as demonstrated by simulation. Figure 13 shows the total reflectivity of the wafer as a function of oxide (layer #1) thickness. A significant sinusoidal variation is observed, with a peak reflection of 50% and a minimum reflection of about 20%. Figure 14 shows the calculated resist linewidth as a function of the oxide thickness, and illustrates that linewidth is hugely affected by small changes in thickness. Comparison of Figure 13 and 14 shows that the linewidth is small (overexposed) when the resist reflection is small, and linewidth is large (underexposed) when the resist reflection is large. The underlying mechanism is that thin film interference is causing the exposure energy within the resist to vary with oxide thickness.

Anti-Reflector Coats or ARCs have been used to reduce such effects, and we will consider an example with our carbon ARC. Figure 15 represents the thin film stack, with the resist on top, the ARC layer #1, the oxide layer #2, and the silicon substrate. Figure 16 shows the resist reflection as a function of oxide thickness. The presence of the ARC has caused the reflection to be roughly 8%, almost independent of oxide thickness, indicating that the exposure energy is not changing much changing oxide thickness. As expected, the linewidth versus oxide thickness curve in Figure 17 is virtually flat. The entire range of the data easily fits within the +-10% linewidth control criterion.

Modern semiconductor processes sometimes have many thin films with variable thickness, and the photoresist film itself can have variable thickness. The ARC layer is generally applicable to reducing the linewidth dependence on the thicknesses of the many layers in the process stack. The C ARC presented in this patent application is a particularly attractive approach, as will be described in detail.

To overcome these problems multilayer resist systems are disclosed herein. In this scheme, a first thick bottom polymer layer with absorption at UV-DUV is spun on the substrate. This layer has both effects to planarize the structure underneath to minimize TFI and to dampen substrate reflections (notching). A second thin Si containing resist layer is spun on top. This thin layer is used as a high resolution imaging layer and, also, after resist development is used as a transfer pattern layer for oxygen reactive ion etching. The bottom layer is not attacked by the developer and the resist top layer is not etched by the oxygen plasma because of its Si content. This process is described in more detail in example 5. An extensive review of multilayer resist technology can be found in "Polymeric silicon-containing resist materials", R. D. Miller and G. M. Wallraff, Advanced Materials for Optics and Electronics, Vol. 4, 95-127 (1994). The currently used bottom layer is a

novolac resist as found in "Bilayer resist approach for 193 nm lithography", Schaedely et al., Proc. SPIE - Int. Soc. Opt. Eng. (USA) Vol. 2724 1996, p344-54. The main problem associated with this "spin on" polymer material is the poor conformality over submicron structures, poor optical tunability, and the chemical interaction at the interface with the imaging resist which may produce variation of the critical dimensions (CD).

If a thick single layer resist is used instead of a bilayer, then mechanical collapse of resist pattern may occur as was found in "Characterization of the resist pattern collapse in a chemically amplified resist", Cha-Won Koh, Cheoul-Kyu Bok, and Ki-Ho Baik, Interface 1996 Proc. p295-302, S.Diego Ca. 1996.

It is an object of the present invention to provide an improved resist.

It is another object of the present invention to provide an improved resist formed from a plurality of layers.

It is another object of the present invention to provide a resist having a plurality of layers wherein the bottom layer is a thick tunable layer.

It is an object of the present invention to propose formation of a bottom planarizing layer by vapor deposition. Vapor deposited films have a vastly increased optical purity and tunability when compared to spin on polymers when used in bilayer and trilayer resist systems.

It is another object of the present invention provide a method of depositing by vapor deposition an a-C:H film which has the required optical properties to form a DUV (365, 248, 193 nm) bottom layer in a bilayer/trilayer resist system. These films have a wide optical tunability, i.e., n and k can be varied by changing process

conditions. These films can be easily patterned anisotropically and removed by oxygen plasma. This method can be easily extended to manufacturing tools currently used in the semiconductor industry.

It is another object to carry out the depositions by vapor deposition in a Ar/hydrocarbon/helium/hydrogen/fluorocarbon/nitrogen/oxygen mixture, preferably with the hydrocarbon being cyclohexane or acetylene and the fluorocarbon preferably being hexafluorobenzene. Higher indexes of refraction are obtained by limiting or excluding hexafluorobenzene (HFB) flow in the plasma chamber, while lower indexes of refraction are obtained by increasing the HFB flows and limiting or excluding the hydrocarbon gas flow. High extinction coefficient *k* are obtained by depositing the films using a high cathode bias voltage, while lower *k* values are obtained by decreasing the bias voltage. Finer optical tunability can be achieved by using proper flow amount of nitrogen and/or oxygen. Hydrogen is used to tune optical properties as well as film durability.

It is another object of the present invention to provide a method of depositing an amorphous carbon film by vapor deposition to be used as a bottom layer in a bilayer resist system with optical properties optimized to minimize reflections occurring at the substrate and at the resist/bottom layer interface. This bottom layer is then acting as a thick planarizing antireflective coating (ARC) which also minimize thin film interference. The process gas chemistry and the process parameters in general are uniquely optimized to achieve the required optical properties.

It is another object of the present invention to provide a method of depositing by vapor deposition a thick ARC layer where the refractive index *n* and the extinction coefficient *k* can be varied through the depth of the film, so as to form an improved antireflector. An example will be shown where the ARC layer is broken into three

distinct layers with different optical properties. We show that this layer has very low reflection, and high tolerance to changes in process. Our deposition techniques can also be applied to a layer where the optical properties are continuously graded through the depth of the film, as has been described by Tanaka et al. in SPIE Vol. 2726, p. 573 (1996). More importantly, if *n and k* of the thick ARC layer is perfectly matched to the adjacent layers, technically, there will be no reflections greatly improving CD control.

The teaching of all referenced cited in this application are incorporated by reference herein.

SUMMARY OF THE INVENTION

A broad aspect of the present invention is a multilayer resist system and method of fabrication thereof.

A more specific aspect of the present invention is a multilayer resist system and method of fabrication by vapor deposition of an a-C:X:H film with tunable optical properties where X is fluorine, nitrogen oxygen, and Si.

Another more specific aspect of the method and structure according to the present invention is depositing a hydrogenated carbon film by vapor deposition from a hydrocarbon/fluorocarbon/hydrogen plasma with optional small amounts of nitrogen and/or oxygen such as about 1 sccm per deposition. The films produced herein have the index of refraction *n* and the extinction *k* coefficient that can be independently tuned at 365, 248, 193 nm, making them extremely useful for thick planarizing antireflective coatings. Additionally, the films formed by the present invention can be deposited conformally on topography and when used as a bottom layer in a multilayer resist system they can be readily patterned and removed in

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

oxygen and/or fluorine reactive ion etching process therefore facilitating patterning for chip fabrication.

Another more specific aspect of a method and structure according to the present invention is depositing an amorphous carbon film by vapor deposition which comprises the steps of: admixing of hydrocarbon, fluorocarbon, hydrogen gases, optionally a small amounts of oxygen and/or nitrogen gases; providing a reactor chamber containing a cathode and the substrate; and introducing the above gas mixture into the chamber; and applying an rf bias potential to the cathode to initiate a plasma and deposit the a-C:X:H film on the substrate by vapor deposition.

Another more specific aspect of the structure and method according to the present invention is depositing an amorphous carbon film by using a gas mixture which comprises, hexafluorobenzene, hydrogen, cyclohexane, acetylene which may or may not diluted in He or Ar to reactively deposit a film by vapor deposition. By employing this method, the index of refraction *n* and the extinction coefficient *k* can be independently optically tuned at UV and DUV wavelengths. More specifically, the UV and DUV index of refraction *n* and extinction coefficient *k* can be tuned from about 1.40 to about 2.1 and about 0.1 to about 0.6, respectively, at 365, 248, and 193 nm. Therefore, these films meet all the requirements needed to be used as a thick planarizing bottom layer in a bilayer resist system.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic of a vapor deposition apparatus useful to practice the present invention.

Fig. 2 is a diagram showing swing ratio definition.

Fig. 3 shows reflectance contours (contours of constant reflectance R_2) in function of n and k (top) and k and SiO_2 thickness for a 300 nm bottom layer.

Fig. 4 shows reflectance contours (contours of constant reflectance R_2)in function of n and k (top) and k and SiO_2 thickness for a 500 nm bottom layer.

Fig. 5 shows reflectance contours (contours of constant reflectance R_2) in function of n and k (top) and k and SiO_2 thickness for a 700 nm bottom layer.

Fig. 6 in A shows reflectance contours (contours of constant reflectance R_2) in function of n and k (top) for a 500 nm tunable bottom layer and in B schematically shows the structure of the multilayer resist.

Fig. 7 (top) shows the measured reflectance and the calculated transmittance of a carbon layer about 500 nm thick as described in example 4. (bottom) shows the corresponding computed n and k values.

Fig. 8 (top) shows the measured reflectance and the calculated transmittance of a carbon layer about 1000 nm thick as described in example 4. (bottom) shows the corresponding computed n and k values.

Fig. 9 illustrates the process flow of the resist bilayer system.

Fig. 10 shows SEM pictures of photoresist lines fabricated using the two layer resist process.

Fig. 11 is a table of optical properties of samples according to the present invention.

Fig. 12 shows a simulation of how the resist linewidth varies with exposure energy.

Fig. 13 shows the total reflectivity of the wafer as a function of oxide (layer #1) thickness.

Fig. 14 shows the calculated resist linewidth as a function of the oxide thickness, and illustrates that linewidth is hugely affected by small changes in thickness.

Fig. 15 represents the thin film stack with the resist on top, the ARC layer #1, the oxide layer #2, and the silicon substrate.

Fig. 16 shows the resist reflection as a function of oxide thickness.

Fig. 17 is a linewidth vs. oxide thickness curve.

DETAILED DESCRIPTION

The present invention relates to structures and methods of fabrication thereof. The structure is produced by a method of vapor deposition from a hydrocarbon and/or fluorinated hydrocarbon (fluorocarbon) plasma, a high quality hydrogenated carbon film to be used as a thick planarizing optically tunable bottom ARC in a multilayer, preferably bilayer/trilayer resist system. The film produced by the present invention has a tunable index of refraction and extinction coefficient which can be optionally graded along the film thickness to match the optical properties of substrate and imaging photoresist. The optical properties at UV and DUV and the lithographic features of the film produced by the present invention are vastly superior to those obtained by other polymeric films such as the diazonaphthoquinone-novolac-type photoresist reported by R. D. Miller and G. M. Wallraff, Advanced Materials for Optics and Electronics, Vol. 4, 95-127 (1994). Thus, Si substrates coated with the

thick planarizing amorphous carbon film of this invention drastically reduce thin film interference and substrate reflectivity at UV and DUV wavelengths, which consequently improves CD control.

Fig. 1 is a diagram of a PECVD (plasma enhanced chemical vapor deposition) deposition apparatus 8 which can be used to deposit amorphous carbon film of the present invention. The apparatus includes a reactor chamber 10 having a throttle valve 11 which separates the reactor chamber 10 from a vacuum pump not shown. A cathode 19 is mounted to the reactor chamber 10 and is isolated therefrom by a dielectric spacer 20. The cathode 19 is provided with a resistive heater 17. A substrate 15 is secured to the inner end of the cathode 19. As herein contemplated, the cathode is electrically connected to a radio frequency source 14 which may be regulated and the impedance between the cathode 19 and the radio frequency source 14 is matched by utilizing a match box 13. The electrical return ground is provided by plate 16 which is connected to the reactor chamber 10.

The reactor chamber 10 also contains conduits 20, 21, 22, 23, 24, 25 for introducing various gas materials into the chamber 10 through a shower head 12. For example, the hydrocarbon gases and the pre-mixed hydrocarbon gas mixture are introduced into the reactor chamber 10 through conduits 25 and 26, respectively. The fluorinated carbon gas and the hydrogen gas are introduced into the chamber 10 through conduits 21 and 20, respectively. The reactive gases oxygen and nitrogen are introduced into the chamber 10 through conduits 23 and 22, respectively, while the Ar gas for cleaning the substrate is introduced through conduit 24.

The hydrocarbon gas which may be used in the present invention may be any hydrocarbon compound which is first capable of being gaseous and then able to form a plasma at the reaction condition employed by the present process. The

term hydrocarbon implies that the molecules which make up the compound contains only carbon and hydrogen atoms. In accordance with one embodiment of the instant invention, saturated or unsaturated hydrocarbon compounds may be employed by the present process. By definition, a saturated hydrocarbon compound is a compound whose molecules contain only carbon single bonds while an unsaturated compound is a compound whose molecules contain carbon double or triple bonds.

It is especially preferred embodiment of the present invention that the preferred reactive hydrocarbon and fluorocarbon gases which are employed in forming the amorphous carbon film are cyclohexane and hexafluorobenzene (HFB) optionally diluted in an inert gas. Additionally, it should be recognized that mixtures of hydrocarbon gases such as cyclohexane/acetylene/methane may also be contemplated as the reactive hydrocarbon gas of the present invention.

Gases employed by the present invention have a purity greater than about 95.5%. In a preferred embodiment, the gases have a purity in the range from about 98.5 to about 99.99%. Most preferably, the gases have a purity greater than 99.99%.

The hydrocarbon, fluorocarbon, hydrogen, helium and argon gases are introduced into the chamber by first passing them through separate flow controllers at a sufficient flow to provide a total pressure of Ar, hydrogen, hydrocarbon, fluorocarbon and helium from about 1 mTorr to 1000 Mtorr. To provide the most effective amorphous carbon film it is preferred that the pressure of argon, hydrogen, hydrocarbon, helium mixture be about 1 - 500 Mtorr. The above conditions can also be obtained by premixing the Ar, hydrogen, hexafluorobenzene, hydrocarbon, helium in one or two or three gas cylinder in any possible combination providing the desired gas concentration. More preferably the argon, hydrogen, fluorocarbon and hydrocarbon gases are introduced into the

chamber though separate flow controllers.

Suitable substrates which may be coated with the amorphous carbon film of the present invention include materials such as plastic; metals; various types of glass; magnetic heads; electronics chips; electronic circuit boards; semiconductor devices and the likes thereof. The substrate to be coated may be any shape or size provided that the substrate may be placed into reactor chamber apparatus. Thus, regular or irregular shape objects having any dimension may be used in the present invention. More preferably the substrate is a Si substrate used in the fabrication of semiconductor devices. The substrate is mounted on the cathode holder inside the reactive sputtering chamber of the reactor device. The reactive chamber is then tightly sealed and evacuated until a pressure reading in the range of about 1×10^{-3} to about 1×10^{-7} Torr is obtained. After evacuating the reaction chamber to the desired pressure range mentioned hereinabove, the substrate is then heated to a temperature from 25 to 400 °C. Most preferably, the substrate is held at a constant temperature of about 50 to about 200 °C throughout the entire deposition process.

The substrate material used may or may not be subjected to rf sputter cleaning using the rf cathode on the chamber prior to depositing the amorphous carbon film. Suitable cleaning technique employed by the present invention includes rf plasma cleaning with hydrogen, argon, oxygen, nitrogen or mixtures thereof, performed singly or in a suitable sequential combination.

After achieving the desired pumpdown pressure, the admixed gases are introduced into the reaction chamber at a flow rates of about 1 to 1000 sccm. More preferably the flow rate of the reactant gases is from 1 to 100 sccm and the flow rate of the hydrogen gas is from 1 to 100 sccm. Most preferably, the flow rate of the cycloexane gas is about 5 sccm. The gas is introduced into the reaction chamber

at a pressure of about 5 to 200 Mtorr. It is another preferred aspect of the instant invention that the admixture be introduced at a pressure of about 100 mTorr.

During deposition an rf bias was applied to the substrate mounted on the cathode. The cathode DC self-bias ranged from -10 to -1000 *Volt* throughout the carbon deposition process. This self-bias voltage was acquired by applying the rf power to the cathode. Radio frequency impedance matching was obtained by using an rf matching box. Most preferably, the substrate rf bias voltage was maintained at negative 300 *V* throughout the experiment. More preferably the power density applied to the substrate is from 0.005 to 5 W/cm^2. Most preferably, the power density employed by the present invention is maintained at about 0.62 W/cm^2 throughout the deposition process.

The amorphous carbon film is deposited onto the substrate at a rate such as that an essentially continuous coating of the film on the substrate is obtained. More specifically, by employing the previously mentioned operation parameters, the amorphous carbon film is deposited onto the substrate at a rate of about 20 to 4000 A/*min.* (A is Angstrom). Most preferably, the rate of depositing the amorphous carbon film onto the substrate is at a rate of about *1600* A/*min.*

In accordance with the present invention, the amorphous carbon film thickness deposited on the substrate are from 1000 to 50000 A. More preferably, the thickness of the amorphous carbon film coating is from 3000 to 7000 A. It should be noted that by changing process parameters such as bias voltage, gas flows, and pressure film optical constants can be changed. Herein, film optical constants are defined as the index of refraction *n* and the extinction coefficient *k*. Thus, it is quite possible to make a substrate with defined optical constants by merely diluting the cycloexane or acetylene in Ar or in He or by changing the cycloexane with mixtures of HFB/hydrogen (Table I). The preferred optical constants of the

amorphous carbon film for bottom layer in a bilayer resist system applications prepared by the present process are in the range from about *k=0.1* to *k=0.6* and *n=1.40* to *n=2.1* at a wavelength of 365 and 248 and 193 nm.

Mainly, the amorphous carbon films formed by the present invention can be used as a thick planarizing ideal bottom antireflective coating to be used in a bilayer resist system for UV (365 nm) and DUV (248 and 193 nm) applications. The advantage of a carbon ARC compared to "spin on polymer" is that carbon can be deposited conformally with drastically improved optical purity and tunability and integrity, therefore enhancing linewidth control and performance of integrated circuits.

It is well known that the effective exposure dose in optical lithography varies periodically with resist thickness due to thin film interference. The swing ratio S is defined as the fractional exposure change between an interference maximum thickness and an interference minimum thickness. S is a fundamental measure of the quality of a particular resist process. By reducing the swing ratio to near zero, the resist process is able to tolerate changes in optical phase due to resist and deposited film thickness non-uniformity. The swing ratio can be calculated by the following equation:

$$S=4(R_1R_2)^{0.5}e^{-\alpha D} \quad (1)$$

where R_1 is the reflectance at the resist air interface, R_2 is the reflectance at the top resist/ARC interface, α is the resist absorption coefficient and D is the resist thickness. In this invention, we are mainly concerned in the reduction of the swing ratio by reducing R_2 through the use of a bilayer resist process with optimized

bottom layer ARC. A diagram explaining the significance of the above parameters is shown in Figure 2. In general, bilayer resist systems can be modeled so a to find bottom layer optical parameters (*n* and *k*) as well as optimum thickness. To achieve this, a knowledge of the optical constants of the entire film structure is necessary in order to compute the swing ratio reduction.

In general, ARC thickness *d* varies between 3000 to 7000 **A** depending on film absorption. The extinction coefficient *k* can vary between 0.11 to 0.5. More commonly, the *k* values were between 0.11 and 0.3 at DUV for a 10X reduction in swing ratio. The index of refraction *n* vary between 1.4 to 2.1. More commonly, the *n* values were between 1.65 and 1.90 at DUV.

The following examples are given to illustrate the scope of the present invention. Because these examples are given for illustrative purposes only, the invention embodied therein should not be limited thereto.

EXAMPLE 1

The following example illustrates calculations for obtaining optimum bottom layer parameters of a bilayer system. Parameters are optimized so as to reduce reflections at the resist/bottom layer interface. Computations are based on algorithms which uses the Fresnel coefficients as found in standard textbooks such as Optics, by E. Hecht and A. Zajac, published in 1979 by Wiley, pages 312 and 313. These simulations can be extended to many different structures and they are not limited by the examples given below. The structure simulated in this example is shown in Fig. 3.

The substrate is silicon with an optional SiO_2 layer grown on top (Fig. 3 bottom), followed by a thick bottom layer and the imaging resist. The parameters under

investigation are the oxide thickness and the bottom layer optical constants *n* and *k* and film thickness *d*. The imaging resist index of refraction extinction coefficient *k* and film thickness are fixed and given by *n=1.78, k=0.018* and *d=2000* **A**. In this example three different bottom layer ARC thickness are simulated, *d=3000, 5000, 7000 A*.

Performance of a bilayer system is defined in terms of low (R_2) substrate reflectivity which translates in a reduction of the swing ratio amplitude as defined in Eq. (1). Fig. 3 (top) shows simulated substrate reflectance contour plots (contours of constant R_2) in function of *n* (for ARC layer) and *k* (for ARC layer) for a *3000 A* thick bottom layer (ARC). The horizontal line *k=0.24*, for example, intercepts several reflectance contours 0.007 being the worst case. Since the reflectance of Si at 248 nm is about 0.7 then a swing reduction $\alpha\sqrt{0.7/0.007}=10$ is obtained. Fig. 3 also shows that for a 10x swing ratio reduction a wide range of index of refraction values is allowed from ~1.65 to ~1.96. If a higher swing ratio reduction is necessary then index values around 1.85 are desirable. In general, from these simulations a range of *k* (ARC) values around an optimum value can be obtained with a reduction in the swing ratio by an order of magnitude or more. Fig. 3 (bottom) shows reflectance contour plots of oxide thickness in function of *k* (ARC). As shown above, *for k=0.24, R <= 0.7 %* with a 10x swing reduction.

Fig. 4 shows (Figs. 4A and 4B and 5A and 5B correspond to Figs. 3A and 3B, respectively) simulations results for a 5000 **A** thick bottom layer. Following the same arguments as above, desirable *n* (ARC) and *k* (ARC) values are in the range of 1.70 to 1.90 and 0.15 to 0.22, respectively, for a *R <= 0.3 %* with a 15x swing ratio reduction. Similarly, Fig. 5 shows that a 25x swing ratio reduction can be obtained for a 7000 **A** thick ARC with *n* and *k* values of about 1.84 and 0.11, respectively. It should be noted these contour plots indicate that a wide range of *n* and *k* values can be chosen in order to obtain a significant swing ratio reduction

(≥10x) and the numbers derived above are given for illustrative purposes. Finally, in order to achieve a higher degree of planarization and therefore minimize thin film interference bottom ARC layer should be preferably 5000 **A** thick or higher.

EXAMPLE 2

This example illustrates how a wider process window with a very low swing ratio values can be obtained by tuning the optical properties of the thick bottom layer. A thin adhesion layer about 150 **A** thick with a *n=1.83* and *k=0.295* is first deposited on Si (see table I in Fig. 11). A second layer which is preferably a fluorinated carbon film is deposited on top. This layer is about 5000 **A** thick. In this case the adhesion layer prevents the fluorine of the thick ARC layer from attacking the Si substrate or SiO_2. In general, the lower index of refraction of the fluorinated carbon film helps to match the indexes of Si and SiO_2. A third layer with a index of refraction of about n=1.78 and extinction coefficient of about k=0.21 is deposited on top to better match the optical constants of the imaging resist. The simulated reflectance contours for this structure are shown in Fig. 6. By comparing this tunable structure with the single layer one of Fig. 4 a large improvement in process window is obtained. The area enclosing the reflectance contour 0.001 of the tunable structure is about one order of magnitude higher than the single layer one of Fig. 4. Thus, a swing ratio reduction of about 27 can be calculated using the same arguments of example 1. Table I shows that a wide range of low indexes and high extinction coefficient can be achieved by using fluorinated carbon film.

EXAMPLE 3

The following example is given to illustrate the process of depositing a hydrogenated and fluorinated amorphous carbon film (to be used as a thick bottom

layer ARC) onto a substrate, preferably Si, by plasma enhanced chemical vapor deposition (PECVD) in a cycloexane gas or HFB with optical characteristics similar to the ones simulated in example 1 and 2.

The experiments were carried out for depositing the amorphous carbon film on five or eight inch round Si substrates. The substrates, which were already precleaned, were blow dried with (filtered) nitrogen gas to remove residual particulate before being loaded on the cathode of Fig. 1. Thereafter, the system was evacuated to a base pressure reading of about $1x10^{-5}$Torr or lower. The substrate was sputter cleaned for 1 min at a power density of 0.4 *W/cm²* at 100 *mTorr* Ar pressure to ensure good adhesion of the carbon film to the Si substrates. The amorphous carbon films were deposited from a cycloexane gas at a flow rate of 25 sccm. The cathode power density was 0.62 *W/cm²* resulting in a -317 *Volt* negative self-bias and the pressure was 100 *mTorr*. During the entire deposition process, the substrates were held at 59 °C. If a fluorinated film has to be deposited then the cyclohexane gas can be replaced with the hexafluorobenzene/hydrogen mixture. A summary of the process parameters used are shown in table 1 (Fig. 11). The gases employed by the present process have a purity of greater than about 99.99%. The amorphous carbon film was deposited onto the substrates at a rate of about 215 A/min.

EXAMPLE 4

The following example illustrates how to measure the optical constants *n* (ARC) and *k* (ARC) of the amorphous carbon film deposited by vapor deposited from a cyclohexane gas. This measurement technique can be applied to a variety of different processes and it is not limited by the two example above.

The optical constants were measured using an n&k Analyzer manufactured by n&k

Technology, S. Clara, Ca.. A description of this instrument and its operation can be found in U.S. Patent No. 4,905,170, 1990. They use a method based on broadband spectrophotometry and equations for optical constants derived by Forouhi and Bloomer (Phys. Rev. B, 38, pp. 1865-1874, 1988). Their analysis is based on a physical model for the refractive index, *n*, and extinction coefficient, *k*, applicable to a wide range of semiconductor and dielectric films, and valid over the deep ultraviolet – near infrared wavelength range. The $n(\lambda)$ and $k(\lambda)$ (λ is the wavelength) spectra of any material cannot be measured directly but they are determined from a de-convolution of a reflectance measurements $R(\lambda)$. This measurable quantity depends on film thickness, optical constants of the films and substrate. The "n&k Method" provides an accurate, rapid, and non-destructive way to uncouple a reflectance measurement. Algorithms can be generated that compare the theoretical reflectance with the measured one. From this comparison film thickness, $n(\lambda)$ and $k(\lambda)$ spectra can be determined.

Figs. 7 and 8 (top) show the reflectance spectra (from 900 to 190 nm) measured by the n&k Analyzer of an amorphous carbon layers to be used as a thick ARC deposited by the method of example 3. The films analyzed are about 5000 and 10000 **A** thick. The corresponding n and k values are plotted in Figs. 7 and 8 (bottom). For these particular examples n varies from ~ 1.80 to ~ 1.82 and k from ~0.22 to ~0.25 at 248 nm which is compatible with the reflectance analysis of example 1. The n&k spectra of Figs. 7 and 8 also indicate that acceptable values n and k are obtained at 193 and 365 nm as explained in example 1.
Finally, the calculated transmission curves (Fig. 7 and 8 top) show that from 500 to 700 nm transmittance varies from 20 to 70% for a 10000 **A** thick film and from 32 to 80% for a 1000 **A** thick film. These transmittance values are acceptable for proper mark alignment in multilayer fabrication of semiconductor chips.

EXAMPLE 5

This example illustrates how to form device features of 0.25 μm and below using a bilayer resist system described above. Fig. 9 shows the fabrication process flow. First a thick amorphous carbon film about or greater than 3000 A as described in example 3 is deposited on a Si substrate with optical constants *n* and *k* of about 1.8 and 0.3, respectively. A thin ~2000 A preferably silated photoresist is spun on top and baked for 90 sec at 90°C (Fig.9.1) such as novolaks, polyhydroxy styrenes, substituted polyhydroxy styrenes polysilanes, polysiloxanes, polysil sesquioxanes, etc., specific examples of which are poly(4-hydroxybenzylsilsequioxane, poly(cyclohexylmethylsilane, 2,1,5-naphthaquinone containing polymethylsiloxane and etc. The silated resist is exposed to a 248 nm radiation at a dose of about 38mJ using a Nikon EXX stepper and post-baked at 120 °C for 90 sec. Then the resist is developed for 30 sec in CD26 Shipley developer (Fig. 9.2). Finally, the amorphous carbon film is reactive ion etched in an oxygen plasma at 50W for 15 min at 25 Mtorr of pressure. Here, the silated resist acts as an etch mask since does not etch in oxygen containing plasma (Fig. 9.3). SEM pictures of the etched bilayer structure are shown in Fig. 10. The boundary between the silated resist and the thick bottom arc is clearly visible. Note that the bottom carbon arc etches anisotropically thus maintaining wall verticality. Resist lines of 250 nm are shown in Fig. 10a. The smaller lines printed here are about 175 nm with aspect ratio ≥3 (Fig.10b). The "grass" visible on the substrate come from contamination of the silicon containing resist during oxygen plasma etching and can be removed by an extremely short exposure to a very low density fluorine containing plasma or by using a longer development time prior to the oxygen RIE.

While the invention has been particularly shown and described with respect to preferred embodiment thereof, it will be understood by those skilled in the art that

the foregoing and other changes in form an details may be made therein without departing from the spirit and scope of the invention.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

This Sheet Has Been Replaced



CLAIMS

1. A structure comprising:

a substrate having on at least one major surface, a plurality of surface layers, at least one vapor deposited antireflection coating layer.

2. A structure according to claim 1, wherein said antireflection coating is a bottom layer which is overcoated with a layer of energy active material.

3. A structure according to claim 1, wherein said substrate is selected from the group consisting of a semiconductor, a polymer, a glass, a metal and combinations thereof.

4. A structure according to claim 2, wherein said energy active material comprises silated photoresist in dry sheet form.

5. A structure according to claim 2, wherein there is about 0.001 reflectance at the interface of said energy active material and said bottom layer.

6. A structure according to claim 2, wherein the swing ratio reduction is at least about 25 or greater.

7. A structure according to claim 3, wherein said substrate is a semiconductor comprised of silicon.

8. A structure according to claim 2, wherein said energy active material is selected from a group consisting of compositions which are sensitive in the UV wavelength



THIS SHEET HAS BEEN REPLACED

This Sheet Has Been Replaced

range, compositions which are sensitive in the DUV wavelength range, compositions which are sensitive in the UV and DUV wavelength ranges and combinations thereof.

9. A structure according to claim 2, wherein the index of refraction and the extinction coefficient of said antireflection coating are finely tuned to substantially match those of said energy active material and said substrate at a first interface between said antireflection coating and said substrate and at a second interface between said antireflection coating and said energy active material.

10. A structure according to claim 1, wherein said antireflection coating is comprised of a carbon-containing material.

11. A structure according to claim 9, wherein said antireflection coating is substantially uniform in thickness and optically nonuniform, with a graded index of refraction and with a graded extinction coefficient.

12. A structure according to claim 9, wherein said index of refraction is tunable between from about 1.4 to about 2.1 at 365, 248 and 193 nms.

13. A structure according to claim 9, wherein said extinction coefficient is tunable from about 0.1 to about 0.6 at 365, 248 and 193 nms.

14. A structure according to claim 9, wherein said index of refraction is tuned to about 1.5 at said first interface to substantially match that of the major surface of said substrate, and tuned to about 1.8 at said second interface to match that of said energy active material with which it is in contact.

15. A structure according to claim 9, wherein said extinction coefficient is tuned to

* C L M S *

THIS SHEET HAS BEEN REPLACED

This Sheet Has Been Replaced

about 0.5 at said first interface to match that of said major surface of said substrate, and tuned to about 0.1 at said second interface to match that of the energy active material with which it is in contact.

16. A structure according to claim 1, wherein said vapor deposited material is selected from the group consisting of diamond-like carbon (DLC), fluorinated diamond-like carbon (FDLC), fluorinated hydrogenated diamond-like carbon (FHDLC), nitrogenated diamond-like carbon (NDLC), amorphous fluorinated hydrogenated carbon, amorphous fluorinated carbon, fluorinated tetrahedral carbon, amorphous nitrogenated carbon, amorphous nitrogenated hydrogenated carbon, nitrogenated tetrahedral carbon, and combinations thereof.

17. A structure according to claim 16, wherein said vapor deposited material includes a dopant.

18. A structure according to claim 10, wherein said vapor deposited material is patternable and removable by reactive ion etching in a gas containing oxygen, fluorine, and combinations thereof.

19. A structure according to claim 17, wherein said antireflection coating comprises a single layer film of uniform thickness, said film having an index of refraction of about 1.42 to about 2.1 and an extinction coefficient of about 0.1 to about 0.6 at wavelengths of 365, 248 and 193 nm.

20. A structure according to claim 10, wherein said antireflection coating has an index of refraction in the range of about 1.6-1.9 and an extinction coefficient of about 0.22 at 248 nm, and a uniform thickness of 300 nm.

21. A structure according to claim 20 having a swing ratio reduction of about 10.

* C L M S *

THIS SHEET HAS BEEN REPLACED

This Sheet Has Been Replaced

22. A structure according to claim 10, wherein said antireflection coating has an index of refraction of in the range of about 1.6-1.9 and an extinction coefficient of about 0.15 at 248 nm, and a uniform thickness of 500 nm.

23. A structure according to claim 22 having a swing ratio reduction of about 15.

24. A structure according to claim 10, wherein said antireflection coating has an index of refraction of in the range of about 1.6-1.9 and an extinction coefficient of about 0.12 at 248 nm, and a uniform thickness of 700 nm.

25. A structure according to claim 24 having a swing ratio reduction of about 25.

26. A structure according to claim 11, wherein said gradient index of refraction is about 1.4 to about 2.1.

27. A structure according to claim 11, wherein said gradient extinction coefficient is about 0.6 to about 0.12.

28. A structure according to claim 11, wherein said antireflection coating has a uniform thickness of about 10 to about 10000 nm on a substrate.

29. A bilayer structure wherein a first layer of thick bottom arc layer, having an index of refraction in the range of about 1.5-1.7, an extinction coefficient in the range of about 0.25-0.45, and a thickness of about 300 to 700 nm is deposited on a first major surface of a substrate.

30. A bilayer structure according to claim 29, wherein said two layers of thick bottom arc layer comprise materials selected from the group consisting of DLC, FDLC, FHDLC, NDLC, amorphous fluorinated hydrogenated carbon, amorphous

* C L M S *

THIS SHEET HAS BEEN REPLACED

This Sheet Has Been Replaced

fluorinated carbon, fluorinated tetrahedral carbon, amorphous nitrogenated carbon, amorphous nitrogenated hydrogenated carbon, nitrogenated tetrahedral carbon, and any combination thereof.

31. A bilayer structure according to claim 30, wherein said thick bottom arc layer material includes dopants selected from the group consisting of oxygen, silicon or mixtures thereof.

32. A bilayer structure according to claim 29, wherein a second layer of thick bottom arc layer, having an index of refraction of about 1.8, an extinction coefficient of about 0.21 and a thickness from about 20 to about 100 nm is disposed on a second major surface of the substrate and overlaid with a photoactive material.

33. A multilayer structure wherein the indexes of refraction and the extinction coefficients within at least one layer of thick bottom arc layer are smoothly graded between a lower value to a higher value through the thickness of said layer.

34. A multilayer structure according to claim 33, including the at least one layer of thick bottom arc layer having an index of refraction of about 1.8 and an extinction coefficient of about 0.3 and a thickness of about 2 to about 30 nm.

35. A multilayer structure according to claim 33, including at least one additional layer of thick bottom arc layer having an index of refraction in the range of about 1.5-1.9, an extinction coefficient in the range of about 0.15-0.5, and a thickness of about 100 to about 1000 nm.

36. A multilayer structure according to claim 33, including at least one additional layer of thick bottom arc layer having an index of refraction of about 1.8, an

* C L M S *

THIS SHEET HAS BEEN REPLACED

This Sheet Has Been Replaced

extinction coefficient of about 0.21 and a thickness of about 100 to about 1000 A.

37. A multilayer structure according to claim 33, including the at least one layer of thick bottom arc layer wherein the index of refraction is smoothly graded from about 1.9 to about 1.5.

38. A multilayer structure according to claim 33, including the at least one layer of thick bottom arc layer wherein extinction coefficient is smoothly graded from about 0.15 to about 0.5.

39. A process for fabricating a dry deposited arc layer film on a substrate, comprising:

mounting a substrate on an electrode of a chamber for deposition of said arc layer film;

evacuating said chamber;

precleaning said substrate and heating it;

introducing dry deposited arc layer -producing gasses;

exciting said chamber at a power density and or a time sufficient to deposit an arc layer to form a coated substrate; and

removing said coated substrate from said chamber.

40. A process according to claim 39, wherein said substrate is a semiconductor substrate.

41. A process according to claim 39, wherein said chamber comprises a reactive sputtering chamber.

42. A process according to claim 39. wherein said evacuating said chamber comprises evacuating said chamber to between about 10^{-3} to about 10^{-7} Torr.

* C L M S *

THIS SHEET HAS BEEN REPLACED

This Sheet Has Been Replaced

43. A process according to claim 39, wherein said heating said substrate comprises heating the substrate to a temperature of about 25 to about 400°C.

44. A process according to claim 39, wherein said precleaning said substrate comprises rf sputter cleaning said substrate.

45. A process according to claim 39, wherein said introducing vapor deposited thick bottom arc layer-producing gasses comprises introducing hexafluorobenzene gasses.

46. A process according to claim 45, wherein said step of introducing HFB gases further includes introducing hydrocarbon gasses and adjusting the relative amounts of each, the index of refraction in the thick bottom arc layer being lower with a relative increase of HFB.

47. A process according to claim 45, further including introducing into the chamber during deposition a dopant level of gas selected from the group consisting of hydrogen, oxygen, and any combination thereof.

48. A process comprising the steps of:

providing a substrate;

depositing a thick bottom arc layer over the substrate;

spinning a silated photoresist on top;

baking said resist at 90°C for 90 sec;

exposing to DUV through a photomask and post bake said resist at 120°C for 90 sec;

developing said silated resist to form a resist patterned structure;

reactive ion etching said thick bottom arc layer in an oxygen and or fluorine containing plasma using the patterned silated resist as an etch mask to

* C L M S *

THIS SHEET HAS BEEN REPLACED

This Sheet Has Been Replaced

form lines of 250 nm and below with high aspect ratio.

49. A structure according to claim 1, wherein said substrate is selected from the group consisting of a magnetic head, electronic chip, circuit board, and semiconductor device.

50. A structure comprising a surface having a patterned antireflection coating thereof.

51. A structure according to claim 2, wherein said energy active material is sensitive to energy selected from the group consisting of electromagnetic radiation, particle beams and heat.

52. A structure according to claim 51, wherein said particle beam is an electron beam.

53. A structure according to claim 17, wherein said dopant is selected from the group consisting of oxygen, silicon and combinations thereof.

54. A process according to claim 39 wherein said heating is by means selected from the group consisting of optical, resistive and combinations thereof.

55. A process according to claim 39 wherein said arc layer is deposited at a rate of about 2 to about 200 nm/min., for a total thickness of thick bottom arc layer of about 100 to about 10000 nm.

56. A structure according to claim 1, wherein said at least one vapor deposited antireflection coating has a predetermined index of refraction profile, a predetermined extinction coefficient profile and a predetermined thickness.

* C L M S *

THIS SHEET HAS BEEN REPLACED

This Sheet Has Been Replaced

57. A structure according to claim 1, wherein said at least one vapor deposited antireflection coating is selected from the group consisting of a coating deposited by plasma deposition, sputter deposition, ion beam deposition, evaporation and combinations thereof.

58. A structure according to claim 1, wherein said at least one vapor deposited antireflection coating is finely optically tuned.

59. A process according to claim 39, wherein said exciting said chamber is to deposit said arc layer by a process selected from the group consisting of plasma deposition, sputter deposition, ion beam deposition, evaporation and combinations thereof.

60. A process according to claim 49 further including introducing a dopant.

61. A process according to claim 39, wherein said arc layer is deposited to have a controlled thickness, index of refraction and extinction coefficient.

62. A process according to claim 1, wherein at least one of said index of refraction and said extinction coefficient have a non-uniform profile.

* C L M S *

THIS SHEET HAS BEEN REPLACED