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An ultrahigh vacuum complementary metal oxide silicon compatible nonlithographic system to fabricate nanoparticle-based devices

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Nanoparticles of metals and semiconductors are promising for the implementation of a variety of photonic and electronic devices with superior performances and new functionalities. However, their successful implementation has been limited due to the lack of appropriate fabrication processes that are suitable for volume manufacturing. The current techniques for the fabrication of nanoparticles either are solution based, thus requiring complex surface passivation, or have severe constraints over the choice of particle size and material. We have developed an ultrahigh vacuum system for the implementation of a complex nanosystem that is flexible and compatible with the silicon integrated circuit process, thus making it suitable for volume manufacturing. The system also allows the fabrication of Ohmic contacts and isolation dielectrics in an integrated manner, which is a requirement for most electronic and photonic devices. We have demonstrated the power and the flexibility of this new system for the manufacturing of nanoscale devices by implementing a variety of structures incorporating nanoparticles. Descriptions of this new fabrication system together with experimental results are presented in this article. The system explains the method of size-selected deposition of nanoparticles of any metallic, semiconducting, and (or) insulating materials on any substrate, which is very important in fabricating useful nanoparticle-based devices. It has also been shown that at elevated substrate temperature, a selective deposition of the nanoparticles is observed near the grain-boundary regions. However, in these natural systems, there will always be low and favorable energy states present away from the grain-boundary regions, leading to the undesirable deposition of nanoparticles in the far-grain-boundary regions, too. © 2008 American Institute of Physics. [DOI: 10.1063/1.2885042]

I. INTRODUCTION

Metallic and semiconducting nanoparticles have great importance for the implementation of a large variety of new electronic and optical devices with improved performances, which include quantum dot lasers, light emitting diodes, single electron transistors, and quantum computing devices. For the implementation of such devices, some of the necessary components are (a) nanoparticles, (b) contact metals, and (c) isolation and/or tunneling dielectrics. While a number of devices based on nanoparticles have been proposed, their successful implementation has been limited due to the lack of appropriate processes that are suitable for volume manufacturing. It is widely believed that for nanoparticle-based devices to be commercially viable, at least in the near future, the fabrication process should be compatible with the silicon integrated circuit (IC) process, in particular, the complementary metal oxide silicon (CMOS) process. Hence, the availability of a nanofabrication technique that is compatible with the silicon CMOS IC process is expected to greatly increase the manufacturing potential of nanoparticle-based devices. For most electronic and photonic devices, it is typically required that the nanoparticle dimensions be in the 1–20 nm range with size variations of 10% or less. Cur-

rent lithographic techniques are not suitable for the implementation of such nanoparticles, and nonlithographic techniques are being increasingly used for their fabrication.^{1,2} However, most nonlithographic techniques are based on natural self-organization processes and suffer from lack of flexibility or lack of engineering control. Among the current nonlithographic techniques, solution based techniques are predominant.^{3,4} While such solution based techniques are capable of producing nanoparticles with the required dimensions and size distributions, they require complex surface passivations involving organic capping molecules to prevent aggregation. These capping molecules modify the electrical surface properties of the nanoparticles, making charge injection/extraction difficult. In addition, the solution based synthesis techniques are not compatible with solid-state device technology, the predominant manufacturing process for electronic and photonic devices, which makes the implementation of Ohmic contacts and isolation dielectrics difficult. The problems associated with solution based methods can be addressed to some extent by using nonlithographic fabrication techniques based on physical vapor deposition of nanoparticles;^{5–9} however, most of these techniques have severe constraints in terms of nanoparticle size, material, location, and choice of substrate. A versatile nanofabrication technique that is capable of producing high purity nanoparticles with control over particle size and flexibility in terms of nanoparticle material and the choice of substrate, together

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with the capability for *in situ* deposition of Ohmic contact and isolation dielectric materials, will be an important step toward the commercial manufacturing of a variety of nanoparticle-based electronic and photonic devices.

In this paper, we describe a system we have developed for the implementation of nanoparticle-based electronic and photonic devices that addresses the above issues. Nanoparticles as well as other device components are fabricated in an ultrahigh vacuum environment in order to obtain high material purity and improved interface properties. The system can deposit nanoparticles of any metal, semiconductor, or insulator with dimensions as low as 1 nm with less than 5% size variation on any kind of substrate. The uniqueness of this system is that besides the nanocluster source, it consists of an electron-beam evaporation system as well as a pulsed dc sputtering unit installed in the same system. Thus, *in situ* deposition of Ohmic contacts and isolation dielectrics can be performed in an integrated manner. In addition, the deposited nanoparticles can be embedded within or coated with metallic, semiconducting, or insulating layers without breaking the vacuum. Thus multilayered compound nanoscale structures can be created, which have diverse applications in the fields of nanoscale detectors, nano-optics, nanosensors, field emitters, etc.^{10–14} The primary strength of this system is that the equipment and the process are compatible with the silicon CMOS IC process lines, thus making this technique suitable for volume manufacturing.

II. EXPERIMENTAL

A. Description of apparatus

The nanodeposition system is an UHV unit designed specifically for the deposition of nanoparticles. It is based on the following:

- (1) A nanoparticle deposition unit which is used to generate nanoparticles of any metal, semiconductor, or insulator of preselected size with particle diameter as low as 1 nm and less than 5% size variation to deposit on any arbitrary substrate.
- (2) An Ohmic contact metallization unit, which is a standard four-pocket minielelectron-beam evaporator, designed for use in UHV environment. It allows the *in situ* deposition of four different metals (and also insulators) with less than 5% thickness nonuniformity. It provides the capability to evaporate high melting-point materials in a controlled manner at rates between <1 monolayer/min to over 5 nm/min. This is achieved by the use of electron-beam-induced heating of the target material to the temperature at which the desired evaporation rate is reached.
- (3) An isolation dielectric deposition unit, which is an UHV magnetron sputter cathode with a pulsed dc source, capable of depositing thick or thin isolation dielectrics (as well as metallic and semiconducting films) of less than 3% thickness nonuniformity.

In the nanodeposition system, the nanoparticle deposition unit, the Ohmic contact metallization unit, and the isolation dielectric deposition unit are all housed inside an ultrahigh vacuum (10^{-10} torr) chamber to ensure high purity

(a)

(b)

FIG. 1. (Color online) (a) Schematic diagram of the nanodeposition system showing the different parts of the system. (b) A picture of the nanodeposition system.

and good surface properties of the nanoparticles. The system also includes standard pumping and cooling systems, gas feedthroughs, a fast entry sample load lock for transferring the substrate to and from the ultrahigh vacuum chamber, internal bakeout, a quartz crystal monitor, and substrate rotation and heating (up to 800 °C) capabilities. A schematic diagram of the positions of all these components on the system are shown in Fig. 1(a) and an actual picture of the system is shown in Fig. 1(b). The nanoparticle unit consists of the main chamber (M), nanocluster source (N), and quadrupole mass filter (QMF), described later. The deposition is done in the main chamber (M), which is always kept under ultrahigh vacuum condition (10^{-10} torr). The nanocluster source (N) is connected to the main chamber via quadrupole mass filter (QMF). The e-beam evaporator (Eb) and magnetron-sputtering unit (SP) are also connected to the main deposition chamber with standard shutter arrange-

FIG. 2. Schematic diagram of the nanocluster source.

ments. Therefore this versatile equipment can be used to fabricate complex nanosystems incorporating nonlithographic nanoparticles of preselected uniform size distribution, Ohmic contact metals, and isolation dielectrics. It also allows the creation of layered structures of nanoparticles of different dimensions separated by metal or dielectric layers.

An important objective in the development of the nanodeposition system was commercial viability of the nanoparticle-based devices. Since it is widely believed that for nanoparticle-based devices to be commercially viable, at least in the near future, the fabrication process has to be compatible with the silicon IC CMOS process, special attention was given to make all processes in the nanodeposition system be silicon IC compatible. While electron-beam evaporation and pulsed dc sputtering are standard techniques used by the silicon IC industry, the selection of the nanoparticle source required serious considerations. The nanoparticle unit in the nanodeposition system is based on a nanocluster source developed by Oxford Applied Research Inc.¹⁵ that is silicon IC compatible as well as provides the desired flexibility for nanoparticle deposition.

Also, the nanodeposition system is a modular equipment that can be expanded to include other units and functionalities such as for the synthesis of carbon nanotubes and semiconductor epilayers, thus making the system more versatile to fabricate diverse nanostructures. The different components of the nanodeposition system are briefly described below.

1. Nanocluster source

The nanocluster source consists of a dc magnetron-sputtering unit, an aggregation region, an aperture through which nanoclusters are channeled to the QMF, gas feedthroughs, cold trap and water cooling systems, differential pumping arrangements, and a linear motion drive to adjust the length of the aggregation region. A schematic diagram is sketched in Fig. 2. The system is specifically designed for UHV environment. The dc magnetron-type discharge is used to generate clusters from the target, connected to the magnetron assembly. The magnetron is designed for high operating pressure and high sputter rate. The magnetron-based source has the advantage over all other types of cluster source in terms of the wide cluster-size

FIG. 3. Schematic picture of the working principle of the QMF. The left-hand-side curve shows the qualitative picture of a broad size distribution of nanoparticles, whereas the right-hand-side curve depicts the narrow size distribution of nanoparticles after filtration through the QMF.

range, which varies from a fraction of a nanometer to a few tens of nanometers. The variation of the cluster size is dependent on several parameters, such as the length in which the clusters aggregate, the power to the magnetron, the flow rate(s) of the aggregation gas(es), the temperature and pressure of the aggregation region and type(s) of the aggregation gas(es) being used, etc. Another important feature of the nanocluster source is the presence of an ionized cluster in the aggregation region, which is suitable to form highly adherent and uniform coatings even on the insulating substrates by the so-called technique of energetic cluster impact. Typically, sputtered clusters are cooled and swept through the liquid nitrogen cooled aggregation region by argon and (or) helium gases, where these clusters nucleate to form a distribution of nanoclusters of various sizes as shown in Fig. 2. The residence time within the aggregation zone can be varied by varying the length of the aggregation region with the linear motion drive and (or) gas-flow rates. By controlling these parameters, so also the residence time, one can control the distribution of the nanocluster size within the aggregation region. Several theoretical and experimental works have been done previously to explain the growth of the clusters within the aggregation region.^{16–18} Generally, the nanocluster size follows a normal (Gaussian) distribution, with a significantly large standard deviation, as shown in the left hand diagram of Fig. 3. Therefore, if these nanoclusters are allowed to deposit on substrates within the main deposition chamber without using any filter, the size variation of the deposited nanoclusters will also be quite significant. However, fabrication of a useful nanodevice requires uniformly distributed nanoparticles with well-defined sizes. Hence, a size selector is essential to select nanoclusters of specific size from the distribution. That is why the QMF is being introduced between the nanocluster source and the main deposition chamber, which acts as a band pass filter to allow nanoparticles of preselected size.

FIG. 4. QMF schematic diagram showing the position of the rods.

2. Quadrupole mass filter

The quadrupole mass filter, intercepted between the aggregation region and the main deposition chamber [as shown in Fig. 1(a)], is used to analyze, electrostatically manipulate, and filter charged nanoparticles from the nanocluster source. It has been designed specifically for the purpose of high-resolution measurement and manipulation and filtering of nanoclusters between 50 and 3×10^6 amu rather than only to detect the presence of elemental or low-mass compound materials by currently available quadrupoles. A schematic representation of the working principle of the QMF is shown in Fig. 3. Nanoclusters of wide size variation (shown at the left hand side of the figure by the normal distribution with a large standard deviation) coming out of the nanocluster source are filtered by the QMF to allow clusters of a preselected specific size with very sharp distribution (as shown in the right hand side curve). Physically, introduction of the QMF is nothing but selecting a specific value of the particle size (say, x_1) from the normal distribution, which is represented by the thin slice around x_1 , shown in the left hand side curve of Fig. 3. The width of the slice, Δx , depends on the resolution of the QMF.

The actual construction of a QMF is schematically shown in Fig. 4. It consists of four cylindrical rods, with alternating voltages applied to the opposite pairs. Nanoclusters of various sizes from the aggregation region enter into the QMF through the entrance aperture, which shields the cluster beam from the end of the quadrupole rods and also helps define the beam. The cluster beam is then allowed to move through the quadrupoles along the axes of the rods. Positive and negative ac voltages are applied to the opposite pairs of poles of the QMF, respectively, and the cluster ions are selected according to their charge-to-mass (e/m) ratio. Ionized clusters with different e/m ratios follow different spatial trajectories due to the external alternating electric field and, thus filtered accordingly. Ideally, a QMF consists of a set of four parallel electrodes with hyperbolic cross sections, with potentials of $\pm A/2$, applied across them, as shown in Fig. 5(a). This structure gives rise to a two-dimensional hyperbolic field, $E(x, y) = A[x^2 - y^2]/2r_o^2$, where $2r_o$ is the shortest distance between the rods (r_o is also called the characteristic radius). Driven by an alternating potential,

(a)

(b)

FIG. 5. (a) Cross-sectional schematic view of an ideal quadrupole consisting of a set of four parallel electrodes with hyperbolic cross sections. (b) Cross-sectional view of a practical quadrupole geometry with cylindrical rods.

$A = \alpha + \beta \cos(2\pi\nu t)$, this field will provide mass-dependent focusing of ionized clusters passing along the central line of the QMF. Practically, hyperbolic shaped electrodes are very difficult to produce; hence cylindrical rods are used with good approximations to the theoretical profile by considering electrode radius r_e as 1.148 times larger than the inscribed circle, r_i , as shown in Fig. 5(b). The parameters which can be varied to allow clusters of particular mass (so also diameter, assuming spherical particles) to pass through are the amplitude of the ac voltage (β), frequency (ν) and dc component of the ac applied (α). The ratio α/β , called resolution, defines the cluster mass (or diameter) band transmitted through the filter. The higher the value of α/β , the narrower the band transmitted through the filter is. Details of the design and working principle of the QMF are furnished in various literatures.^{19,20} Theoretically, the resolution of the QMF can be better than 0.01%, but in reality, the optimum resolution is determined by a number of other parameters including the mechanical construction (diameter, tolerance, length, and alignment of the poles), variations in the initial cluster ion energy, electrical imperfections, etc.¹⁹ Therefore, the typical usable cluster-size resolution of the system becomes $\sim 2\% - 6\%$. Hence, as explained in Fig. 3, clusters of large size distribution generated in the nanocluster

source are filtered through the QMF to give a narrow size distribution centered on a preselected cluster size. The full width at half maximum of this distribution depends on the resolution of the QMF. Another important feature of this system is the X , Y deflection plates present after the QMF (not shown in Fig. 4). Neutral particles present in the incoming flux, which will not be affected by the QMF, can be separated from the ionized clusters by applying suitable voltages in the X , Y deflection plates, thereby deflecting the size-selected charged nanoparticles to the substrate mounted at an angle.

B. Deposition procedure

We have deposited nanoparticles of metallic (Cu), semi-conducting (Si), and compound (CdS) materials. The magnetron power in the nanocluster source, flow rate of the sputtering gas (Ar), substrate temperature, and deposition time were varied to examine the variation in the size distribution of deposited nanoparticles on various substrates. Bare Si, Al-coated Si, indium tin oxide-coated plastic, and commercially available glasses were used as substrates for the deposition of nanoparticles. However, most of the results furnished in this article are for Al-coated Si substrates. The Al is used as a sublayer (~ 500 nm thick) mainly for the contrast between the Si nanoparticles and substrate during electron microscope imaging. If we have deposited Si nanoparticles on bare silicon substrates, then it might become very difficult to distinguish between the nanoparticle and the substrate. That is why we have deposited a sublayer of aluminum on the Si substrate. For Cu and CdS nanoparticle growth, bare silicon substrates could have been used, but we have used a similar kind of substrates throughout the experiment to make parity between the images of different materials. In most cases, the substrate temperature was kept at ambient condition to determine the efficiency of the QMF as a size selector, but in some specific experiments, we have deposited the nanoparticles in elevated substrate temperatures of 60 and 80 °C to investigate the substrate effect on the deposited nanoparticles. Also the base pressure of the deposition chamber was held at the 10^{-10} mbar range. Details of the deposition conditions were described elsewhere.^{21,22} The substrates were cleaned by the standard substrate cleaning procedures. The parameters for the QMF were so chosen to deposit nanoparticles of 5–15 nm sizes. Also we have qualitatively examined the efficiency of the QMF by depositing nanoparticles with and without the QMF turned on. The size variation of the deposited particles was then calculated and compared with each other to get an idea on the size selectivity of the QMF.

The characterizations of the nanoparticles were done by field-emission scanning electron microscopy (FESEM) (JEOL JSM 6700F) and high-resolution transmission electron microscopy (HRTEM) (TECNAI G² S-TWIN).

III. RESULTS AND DISCUSSION

Figure 6(a) represents the FESEM image of Cu nanoclusters deposited on Al-coated Si substrates with QMF off condition. Figure 6(b) represents the same with QMF turned

FIG. 6. (a) FESEM image of Cu nanoparticles at 70 SCCM Ar flow rate with QMF turned off. Inset: Size distribution of the nanoparticles. (b) FESEM image of Cu nanoparticles at 70 SCCM Ar flow rate with QMF turned on and set to 10.0 nm size selection. Inset: Size distribution of the nanoparticles.

on and set to 10.0 nm of particle selection. In both cases, the Ar flow rates were 70 SCCM (SCCM denotes cubic centimeter per minute at STP). Similarly, Figs. 7(a) and 7(b) represent the Cu nanoparticles with QMF off and on conditions, respectively, at 50 SCCM Ar flow. Figures 8(a) and 8(b) show the same for 30 SCCM Ar flow rate. In these cases also, the QMF is set to 10.0 nm particle selection. The deposition time and aggregation length are kept identical in all cases. The insets of all the figures represent the size distribution of the nanoparticles obtained from the respective images. These figures are basically used to determine the resolution and accuracy of the QMF. The size distributions of nanoclusters with QMF off, shown in the insets of Figs. 6(a), 7(a), and 8(a), are determined from the image analyses of FESEM micrographs, assuming the cluster area to be the projection of a spherical particle. The column charts are the

(a)

(b)

FIG. 7. (a) FESEM image of Cu nanoparticles at 50 SCCM Ar flow with QMF turned off. Inset: Size distribution of the nanoparticles. (b) FESEM image of Cu nanoparticles at 50 SCCM Ar flow with QMF turned on and set to 10.0 nm size selection. Inset: Size distribution of the nanoparticles.

experimental data measured from the respective figures. The data are well approximated by Gaussian distributions with peak diameters of 12.8, 18.1, and 22.0 nm for 70, 50, and 30 SCCM, respectively. The size variation, obtained from the distributions are found to be around 16.84%–27.30%. Physically, these distributions are the representative of the cluster distributions present within the aggregation region of the nanocluster source under the applied operating conditions. With changing the operating conditions, such as sputtering power, pressure, gas flow, aggregation length, etc., one can change the peak value as well as the distribution of clusters, and thus calibrate the nanocluster source for optimum performance. Several theoretical explanations and modeling have been proposed previously to explain the growth of the clusters within the aggregation region.^{16–18,23–27} In our previ-

ous work,²² we have studied in detail the effect of various deposition conditions (such as sputtering pressure, gas-flow rate, length of the aggregation region of the cluster source, etc.) on the cluster-size distribution within the nanocluster source and tried to correlate the results with the existing models, and thereby calibrated the nanocluster source for optimum performance. Generally the sputtering-aggregation process involves the typical magnetron-sputtering vaporization of target materials followed by an inert gas condensation to form clusters of varying sizes. As mentioned earlier, the size distributions of the clusters typically follow normal distribution and the peak cluster sizes of the distributions depend on several factors, which include gas-flow rate, length of the growth region, deposition pressure, etc. Experimentally, we have deposited Cu and Si nanoparticles at

(a)

(b)

different Ar flow rates with QMF off conditions. The aggregation length and the sputtering power were kept constant throughout the experiment. The size distributions of the deposited nanoclusters are then analyzed from the FESEM micrographs in a similar way as described earlier. These data are then matched with the existing model used by previous authors¹⁷ and the system was calibrated accordingly. In Table I, the theoretical mean cluster size obtained from the existing model is compared with the experimentally determined peak cluster size from FESEM micrographs (see Figs. 6–9). The values are found to be quite in agreement with the theoretical values. The results are significant since they demonstrated that proper optimization of operation conditions can lead to the desired cluster sizes as well as desired cluster-size distributions. A detailed discussion on this process is described elsewhere.²²

FIG. 8. (a) FESEM image of Cu nanoparticles at 30 SCCM gas flow with QMF turned off. Inset: Size distribution of the nanoparticles. (b) FESEM image of Cu nanoparticles at 30 SCCM gas flow with QMF turned on and set to 10.0 nm size selection. Inset: Size distribution of the nanoparticles.

In this paper, we have used the QMF mainly as a size selector to select nanoparticles of predetermined values from the cluster distribution generated in the nanocluster source. The insets of Figs. 6(b), 7(b), and 8(b) represent the particle size distribution of Cu nanoparticles with QMF turned on and set to 10.0 nm size selection, as mentioned earlier. The distributions are well fitted with a Gaussian curve with peak-particle diameters of 9.90, 9.84, and 9.96 nm for 70, 50, and 30 SCCM Ar flow rates, respectively. The deviation of the particle size from the peak value is found to be around 5.0%–6.0%, which is quite low with respect to the variations obtained without the QMF ($\sim 16.8\%$ – 27.3%). This shows the strength of the mass filter to get an accurate, narrow size distribution of nanoparticles. It is also to be noted that the cluster density for 70 SCCM gas flow is much greater than

TABLE I. Comparison of the theoretical and experimental average particle sizes and size-variations of as-deposited Cu, Si, and CdS nanoparticles for different QMF conditions and gas-flow rates. Theoretical values of the nanocluster size are obtained from Ref. 22.

QMF condition	Material		QMF off			QMF on		
			Cu	Si		Cu	Si	CdS
Gas-flow rate (SCCM)	70	Theoretical cluster size (nm)	11.80	42.0	Preselected particle size (nm)	10.0	10.0	15.0
		Experimental cluster size (nm)	12.80	38.6	Experimental particle size	9.90	10.14	17.1
		Size variation (%)	22.3	21.0	Size variation (%)	6.0	6	12.2
	50	Theoretical cluster size (nm)	20.40	47.0	Preselected particle size	10.0	10.0	15.0
		Experimental cluster size (nm)	18.10	44.0	Experimental particle size	9.84	10.16	17.6
		Size variation (%)	16.8	18.4	Size variation (%)	5.8	6.8	13.8
	30	Theoretical cluster size (nm)	26.0	60.50	Preselected particle size	10.0	10.0	15.0
		Experimental cluster size (nm)	22.0	55.0	Experimental particle size	9.96	9.8	18.0
		Size variation (%)	27.3	24.0	Size variation (%)	5.1	...	...

that for flow rates of 50 SCCM and less, as observed in Figs. 6–8. This shows that the cluster count is nonlinearly related to the gas-flow rate, as indicated and explained in various literatures.^{23–27} The experimental peak diameter of Cu nanoparticles along with the size variations at different Ar flow rates is furnished in Table I.

We have also deposited semiconducting Si nanoparticles on Al-coated Si substrates at various Ar flow rates. Figures 9(a) and 9(b) show FESEM micrographs of as-deposited Si nanoclusters for Ar flow rates of 70 SCCM with QMF off and on conditions, respectively, under identical deposition time. The insets show the respective size distributions of the as-deposited nanoclusters. For Fig. 9(b), the QMF was set to 10.0 nm size selection. The mean cluster size in Fig. 9(a) (QMF off condition) is found to be 38.60 nm with 21.0% size variation. With QMF turned on [Fig. 9(b)], the distribution is found to give a peak-particle size of 10.14 nm and a size variation of as low as 6.0% compared to the large variation shown in Fig. 9(a) with QMF turned off (21.0%, as mentioned earlier).

Figures 10(a) and 10(b) show the deposition of Si nanoparticles with QMF on condition and set to 10 nm size selection. The gas-flow rates in these cases are 50 and 30 SCCM, respectively. As expected, with lesser flow rates, the numbers of particles on the substrates are found to be lower. This is obvious because at lower flow rates, particle flux should be lower, so also the number density of deposited

particles would be lesser for identical deposition times. In a similar way, the distribution of the nanoparticles in Fig. 10(a) depicts a peak-particle diameter around 10.16 nm with a low size variation of 6.8% (shown in the inset). For 30 SCCM Ar flow rate, the distribution cannot be obtained due to the very less number of particles [as shown in Fig. 10(b)] statistically, which will not produce a true representation of the entire distribution. Therefore, in this case, the individual particle sizes are determined from the image and averaged out to get the representative particle diameter, which is found to be around 9.8 nm. It is to be noted that for Ar flow rates of 50 and 30 SCCM, the FESEM images of Si nanocluster with QMF off conditions had also been obtained [not shown here, but the images are similar to Fig. 9(a) with a lesser number of cluster density]. These images also showed large variations in cluster size, present in the nanocluster source under the corresponding operating conditions (corresponding data are furnished in Table I).

We have also varied the deposition time of the nanoparticles to control the number density of the particles. Figure 11(a) shows the deposition of a very few (just one or two) Si nanoparticles on the substrate (one of them is shown by the arrow) at a lower deposition time. This describes the important feature of the deposition system that the number density of nanoparticles can be precisely controlled by accurately monitoring the deposition time.

Another interesting observation has been made when we

(a)

(b)

FIG. 9. (a) FESEM image of Si nanoparticles at 70 SCCM Ar flow rate with QMF turned off. Inset: Size distribution of the nanoparticles. (b) FESEM image of Si nanoparticles at 70 SCCM Ar flow rate with QMF turned on and set to 10.0 nm size selection. Inset: Size distribution of the nanoparticles.

attempted to increase the temperature of the substrate during deposition to observe any substrate effect on the nanoparticles. We surprisingly observed that at substrate temperatures of 60 and 80 °C, there is a trend of preferential deposition of nanoparticles near the grain-boundary region. Figure 11(b) shows the as-deposited Si nanoparticles at a substrate temperature of 60 °C. As clearly visible in the image, quite a few numbers of particles are found to sit near the grain-boundary region (indicated by arrows), showing some preferential deposition near the grain boundary. In general, grain-boundary regions of thin films always consist of various surface states with considerable energy distributions. Increase in substrate temperature sometimes produces large energy variations within these regions, leading to favorable energy conditions for the deposited nanoparticles,

and therefore, a preferential deposition of nanoparticles near the grain-boundary region is observed at elevated substrate temperature. At the higher substrate temperature of 80 °C [Fig. 11(c)], we have observed a natural patterning of the nanoparticles across the grain boundaries, as shown by arrows in Fig. 11(c). Although there are some nanoparticles deposited away from the grain boundaries, as evidenced from the figures, this is mainly because in these natural systems, there will always be low and favorable energy states present away from the grain-boundary regions, leading to the deposition of nanoparticles in these regions, too. Also some undesired agglomerations of nanoparticles into bigger clusters are observed due to the higher substrate temperature, but this result is interesting in the sense that if one can have a film with smooth, periodic surface energy variation, then a

(a)

(b)

FIG. 10. FESEM images of Si nanoparticles deposited on Al-coated Si substrates for Ar flow rates of (a) 50 SCCM and (b) 30 SCCM with QMF on condition. The size-selection parameter in QMF was set to 10.0 nm in both cases. The inset of (a) shows the corresponding size distribution of the nanoparticles.

natural patterning of quantum dots can be achieved by non-lithographic technique. To gain more control over the position-selective deposition, an external voltage-driven substrate energy variation may produce selective deposition of the nanoparticles as these nanoparticles are charged (mentioned earlier), which is the further course of our work.

So far, we have furnished the results of the deposition of elemental materials by the nanodeposition system. Generally, cluster formation and mass selection for elemental materials are a little bit straightforward. This is mainly because of the presence of a considerable amount of ionized clusters in elemental materials, and therefore, electrostatic manipulation of the ionized clusters within the mass filter is easier. On the other hand, clusters of compound materials consist of a fair amount of neutral particles, which would not be affected by the alternating electric field of the mass filter. Therefore, careful application of suitable voltages in the X , Y deflection

(a)

(b)

(c)

FIG. 11. (a) FESEM image of two Si nanoparticles deposited at a very low deposition time. One of them is indicated by the arrow. (b) FESEM image of Si nanoparticles at a substrate temperature of 60 °C, indicating preferential deposition near the grain-boundary (indicated by arrows). (c) FESEM image showing a trend of natural patterning of Si nanoparticles along the grain-boundary region at elevated substrate temperature of 80 °C (indicated by arrows).

plates is needed to separate these neutral particles from the incoming flux. Here we have investigated the deposition of CdS nanoparticles of 15 nm size selection at 30–70 SCCM argon flow. Figures 12(a)–12(c) show the FESEM images of CdS nanoparticles at 70, 50, and 30 SCCM Ar flow rates, respectively. For Figs. 12(a) and 12(b), Al-coated Si substrates were used, whereas in Fig. 12(c), bare Si substrate was used for deposition of CdS nanoparticles. The insets of Figs. 12(a) and 12(b) depict the corresponding size distributions of as-deposited nanoparticles. The average peak-particle sizes obtained for 70 and 50 SCCM Ar flow rates are

(a)

(b)

(c)

FIG. 12. FESEM images of CdS nanoparticles for (a) 70 SCCM, (b) 50 SCCM, and (c) 30 SCCM Ar flow rates. The QMF is turned on in all three cases and set to 15.0 nm size selection. The insets of (a) and (b) show the corresponding size distributions.

17.1 and 17.6 nm, respectively. Also, the corresponding percentage variations of the size of the deposited nanoparticles in the above-mentioned two cases are around 12.2%–13.8%, whereas for 30 SCCM Ar flow rate, the average particle size is found to be around 18.0 nm [here also, due to the less number of deposited particles, the true distribution cannot be obtained, instead, the individual particle sizes are determined from the image and averaged out, as explained previously for Fig. 10(b)]. It is to be noted that a considerable amount of deviation in the experimentally obtained peak-particle size is observed with respect to the preselected value (15.0 nm). Also, the size variation is quite large with respect to that obtained for Cu and Si nanoparticles. These results lead to the conclusion that there are still considerable amounts of

(a)

(b)

FIG. 13. HRTEM images of (a) polycrystalline and (b) single-crystalline Si nanoparticles of 15 nm diameter. The corresponding Fourier transform micrographs are displayed in the insets.

neutral CdS nanoclusters present within the nanocluster region, that are not affected by the electrostatic force of the QMF, and therefore modified the particle distribution. Hence, considerable attention is needed to apply suitable voltages in the X , Y deflection plates to separate these neutral clusters from the incoming particle flux, which is the further course of our research work. Previously, Bromann *et al.*²⁸ reported the deposition of size-selected Ag nanoparticles on Pt substrates by an UHV technique. A quadrupole mass selector was used for the size selection. However, to the best of our knowledge, there is no report on the size-selected deposition of compound materials by an UHV technique.

To investigate the quality of the deposited nanoparticles, HREM analyses were performed. Figures 13(a) and 13(b) show the HRTEM images of polycrystalline and single-crystalline Si nanoparticles, respectively, indicating the high quality of the nanocrystals produced in this process. The average particle diameter is around 15 nm in both cases. Fast Fourier transform micrographs of both the particles are shown in the insets of the respective images. The highly oriented atomic planes are clearly visible and the analyses of the micrographs depict the (111) lattice orientation of the nanoparticles. A closure look into the HRTEM images reveal the presence of some point defects within the high-crystalline nanoparticles, which may be attributed to the sample preparation procedure by ion-milling process for TEM imaging and not to the deposition procedures. In the

Fourier transform micrographs, it appears that some kind of double diffraction is present due to the twist in the crystal lattice,²⁹ and this twist may again be attributed to the sample preparation procedure for TEM imaging. It has been observed that, on an average, one-third of the deposited nanoparticles are single crystalline in nature (for 50 SCCM Ar flow rates), whereas the rest of them are polycrystalline. This is mainly because, in a sputter-gas-aggregation-type system (which is in our case), in general, within the aggregation region, agglomeration of smaller particles to bigger clusters occurs, which causes the nanoclusters to become polycrystalline. The greater the sputtered particles that stay within the aggregation region, the higher would be the probability of agglomeration, which, in turn, leads to a potential increase in the polycrystallinity of the deposited nanoparticles. Therefore, among the various deposition parameters, the mass flow rate and aggregation length are supposed to affect the crystallinity of the deposited nanoparticles to a great extent because these parameters control the time of flight of the sputtered particles within the aggregation region. In our case, we have kept the aggregation length constant throughout the experiment but varied the gas-flow rate and observed that for 50 SCCM Ar flow, only 30%–35% of the deposited nanoparticles are single crystalline, whereas for 70 and 30 SCCM Ar flow rates, these values are 45%–50% and 15%–20%, respectively. A postannealing step and (or) deposition at elevated substrate temperature may significantly enhance the percentage of single-crystalline nanoparticles over polycrystalline ones.

To demonstrate the versatility of our nanodeposition system, we have synthesized another interesting complex nanostructure, where three layers of Si nanoparticles embedded in a thick Ni layer have been fabricated. The nanoparticles in the layers have average sizes of 11, 8, and 5 nm, respectively, separated by 100–150 nm Ni layers and finally coated with another 10–30 nm Ni film to prevent from oxidation. A schematic diagram of the proposed structure is shown in Fig. 14(a) and the corresponding cross-sectional FESEM image of the as-deposited multilayer structure is shown in Fig. 14(b). Three layers are clearly visible in the image separated by Ni films. To observe a significant number of nanoparticles in the cross-sectional view, we have increased the particle density and hence observed agglomeration of nanoparticles to bigger clusters. Similarly, we have also demonstrated the deposition of a layered structure containing stacked layers of CdS nanoparticles separated by thin layers of Al_2O_3 . Five layers of CdS nanoparticles with diameter ranging from 5 to 15 nm were deposited within the layers of Al_2O_3 of thickness of 100–200 nm. Figure 14(c) shows a cross-sectional image of such a layered structure, where different layers and interfaces are clearly visible. Generally, a single layer of nanoparticles may not produce a significant amount of signal for useful applications. On the other hand, increment in the number density of nanoparticles in a single layer would result in the agglomeration of particles to bigger clusters, and thus deteriorate the signal quality. Therefore, multilayered structures of nanoparticles stacked within some insulating layers would produce a significant amount of signal for detection without agglomeration. The FESEM image

(a)

(b)

(c)

FIG. 14. (a) Schematic diagram of a proposed multilayer complex nanostructure consisting of three layers of Si nanoparticles of different sizes embedded in Ni layers. (b) Cross-sectional FESEM image of the as-deposited $\text{Si}_{(\text{nanoparticle})}/\text{Ni}_{(\text{film})}$ multilayer nanostructure. (c) Cross-sectional FESEM image of a multilayer structure consisting of five stacked layers of $\text{CdS}_{(\text{nanoparticles})}/\text{Al}_2\text{O}_{3(\text{film})}$ deposited on Si substrate.

shown in Figs. 14(b) and 14(c) depicts the versatility of our equipment, where multilayer structures can be fabricated with metallic, insulating, and other semiconducting layers and nanoparticles of various thicknesses and sizes, respectively, which have diverse applications in multijunction nanodevices, nano-optics, and nanosensors. Recently, Maheshwari and Saraf³⁰ reported fabrication of a touch-sensitive multistructured device consisting of alternating monolayers of Au and CdS nanoparticles separated by dielectric films, which is very similar to our fabricated multilayer structure. However, this structure was fabricated by a solution based technique. In general, wet-chemical processes are not compatible with current solid-state methods of device fabrication and, therefore, alternative UHV technique is the need of the hour. So our nanodeposition system has the capability to create high efficient complex nanodevices, compatible with cur-

rent solid-state fabrication procedure. Also, in addition, we have recently initiated some experiments of codeposition of nanoparticles and insulators to create coated layers of nanoparticles, which has important applications in light emitting devices and may be implemented (with proper modification) in biosensing applications.

IV. SUMMARY

In summary, we have developed an ultrahigh vacuum, nonlithographic technique for the implementation of complex nanosystems incorporating nanoparticles of metallic, semiconducting, and compound materials, Ohmic contact metals, and isolation dielectrics with specific focus on volume manufacturing. A magnetron-based nanocluster source is used to produce nanoclusters of various sizes from any kind of metallic, semiconducting, and insulating targets. A quadrupole mass filter is used to select nanoparticles of a particular size for deposition on a substrate. The deposited nanoparticles of Cu and Si show only 4%–6% variations in the size after filtration, indicating high resolution of the QMF. The deposition time has also been monitored to control the number density of nanoparticles. Nanoparticles of compound semiconductors such as CdS have also been deposited by this UHV system. HRTEM images of Si nanoparticles show both single-crystalline as well as polycrystalline nature, with highly oriented atomic planes with (111) lattice orientation. The sputter-gas-aggregation-type nanocluster source present in our nanodeposition system, where smaller particles agglomerate to bigger ones, is found to be responsible for the presence of polycrystalline nanoparticles. The deposition parameters, which control the residence time of the nanoparticles within the aggregation region, such as aggregation length, gas-flow rate, etc., are found to affect the single-crystalline nature of the deposited nanoparticles to a great extent. Also, we have synthesized complex multilayered structures incorporating nanoparticles of various dimensions separated by layers of metals or insulators. It is believed that such a multilayered structure is a necessary step toward the practical realization of nanoparticle-based photonic and electronic devices. We have demonstrated the power and the flexibility of this new system and technique for the

implementation of various structures incorporating nanoparticles and are currently working on the implementation of a variety of electronic and photonic devices.

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