The Process of Forming Micropattern Image from "Liquid" Nano Carbon

Khe C. Nguyen, Saigon Hi Tech Park Research Laboratories, HoChiMinh City, Viet Nam; Le Van Thang, Doan Duc Chanh Tin, Tran Viet Toan,Nguyen Thuy Ai, Truong Thuy Le, Luu Tuan Anh, and Dang Mau Chien, Department of Material Science and Engineering, University of Technologies in HoChiMinh City, Viet Nam; Vo Hong Nhan, Department of Material Science and Engineering, University of Can Tho in CanTho City, Viet Nam

Abstract

Surface modification of carbon black with suitable anchor groups has been known to be best fit to the requirements of inkjet colorant.1 We found that surface modified carbon black can be successfully utilized as masking materials for many applications of semiconductor wafer processing. The present study attempts to achieve nano scale particles by attaching the electrolytic groups on the carbon black powder (average particle size 3 um) surface to form a pseudo products called as the "liquid" nano carbon. (LNC) having average particle size down to the range between 20-30nm detected by AFM (Atomic Force Microscopy) tip. As a result, the LNC product exhibits the thin film (400 Ao thick) forming properties without using vacuum techniques and micro patterning capability useful for microelectronic device fabrication.

Introduction

Micro Patterning

a) Lithography is a process of forming engraved patterns on a certain substrate. Generally speaking, micro patterning is the process of laying out the periodic patterns of microcircuits on a semiconductor wafer for the fabrication of microelectronic devices. In the micro fabrication process, the well known photolithography can transfer the micro pattern image from the mask into a photosensitive layer (photo resist) by the light projection in a combination with a mask aligner. This process lays out multi layer of different circuit designs onto one substrate by aligning the alignment marks on the masks with that of the wafer. At the wafer processing end, each completed die is isolated by the die cutting and ready for the next step of packaging into single chip devices.

b) In the micro device processing, carbon material looks promising because of many advantages such as heat resistance, anti reflection, electrical conductivity etc.... However, the greatest challenge still remains in the low cost, simple process of making uniform thin film having desired chemical reactivity required for micro pattern forming. Several efforts attempting to resolve this issues which had been reported are the heat - burned photo resist 's micro patterning,[2] plasma etched carbon black/polymer[3] micro patterning etc... These approaches do not satisfy the quality of the patterns as well as the requirements of cost reduction for production scale.

"Liquid" Nano Carbon

In the present study, we are trying to to take advantage of electrostatic repulsive force to minimize intermolecular interaction between particles in primary aggregate of carbon black and self-stabilized into nano scale particles or nano scale aggregate. USP 5554739 and 5922118,[1] demonstrated unique carbon black material for inkjet colorant application by attaching water soluble anchor group onto it to form super aqueous dispersion stability. The attachment occurs via a diazo coupling reaction using primary amine precursor having the desired functional groups. The average particle size of the commercial product Cabojet 200 and Cabojet 300 is reported in the vicinity of 130nm and these are excellent for inkjet application but not quite a nano material yet.

In our approach, we increased the concentration of electrolytic groups on individual carbon black powder by repeating the diazo coupling reaction on the same materials. This process is called as multiple diazotization. The multiple diazotization on carbon black particles tends to yield nano scale aggregate and nano scale particles. These aggregates shows the impression of "solubility" in strong polar solvents and having nano scale size, thus, the terminology "liquid" nano carbon (LNC) is referred as *multiple diazotized carbon black* product. From now on, the terminology LNC will be used through the report.

Experimental Procedure, Results and Discussions

Preparation of Carbon Black Raw Materials

Carbon black was prepared by burning acetylene gas coming out from the reaction of water with calcium carbide. The fume product is quenched with cooled jacket water and collected in a magnetic stirrer water vessel. The primary aggregate of carbon black was respectively washed with acid, base, organic solvents (toluene, acetone), rinsed with water and baked at 140C at least for 4 hrs in a convection oven.

Multiple Diazotized Carbon Black

The diazotization of the carbon black raw material using sulfanilic acid was prepared referring the previous report.[4] The first diazotization product is named as Diazo 1 and the nth diazotization product is named as Diazo n. Figure 1 exhibits IR spectroscopy chart of the raw material (red), Diazo 1 (blue) and Diazo 4 product (black). One can recognize the difference in IR spectrum of these samples, revealing the effect of multiple diazotization effect. It should be also recognized that the IR absorption peak appeared at the vicinity of 3400-3450 cm^{-1}, representing –OH, all exist in the raw material and the product of Diazo1 and Diazo4. However, the peaks appeared at 1160-1200 cm^{-1} and 1330-1380 cm^{-1}, representing –SO3 and the peaks appeared at the vicinity of 1030-

1080 cm^{-1} and 1110-1150 cm^{-1}, representing –N=N, only clearly appear in the products but not in the raw material. The presence of –SO3 group in the Diazo products confirms the successful attachment of electrolytic group –SO3H or –SO3Na from sulfanilic acid molecule and explains the increased hydrophilicity of the carbon black. Besides the above groups, it is also observed the presence of the absorption peak at the vicinity of 1600 cm^{-1} representing conjugated bond C=C, 2900-3000 cm^{-1} peak representing C-H bonding, 1200-1400 cm^{-1} representing the IR vibration of –OH. Figure 2 exhibits SEM image of the dried powder of various types of carbon black (a) raw material and (b) Diazo 1 product on the same magnification X5000. It is observed that SEM reveals average particle size of 3um for the raw material and roughly 100 -150 nm for the Diazo 1. So it is very clear that the attachment of electrolytic group –SO3H already reduces the average particle size of the raw material down to 20 X. Figure 3 is SEM image of dried powder of Diazo 1 (a) and Diazo 4 (b) in the magnification of 50,000 X. Due to the limited resolution of SEM image, it is barely able to recognize a slight reduction of particle size from Diazo1 to Diazo 4. However, SEM's quantitative analysis only reveals a rough measurement of average particle size of Diazo 4, which is in the range between 50 and 70nm, i.e., particle size reduction 2X from Diazo 1 to Diazo 4.

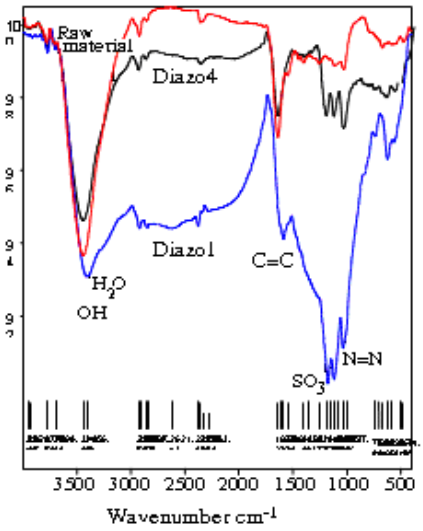


Figure 1. FtIR spectrum of raw material, Diazo 1, Diazo 4

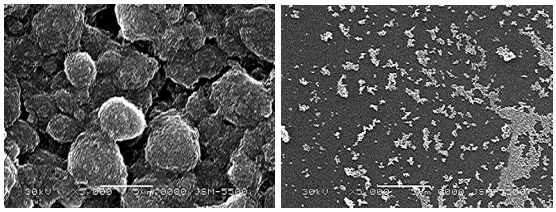
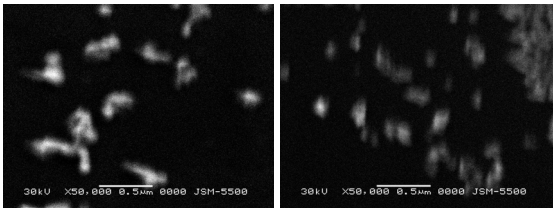


Figure 2. SEM image of dried powder of carbon black (a) raw material (b) Diazo 1. Magnification X5000

Figure 4 shows the AFM (Atomic Force Microscopy, tapping mode services from Poly Insight, LLC) image of Diazo 4 from a dried drop on a glass substrate. It is very clearly that the dried drop is composed of multi particle aggregate and the average size of individual particles is detected to be between 20-30nm. However Figure 5 shows AFM image of stack of aggregate flushed with a few drops of water and one can see the isolation of single particle. These data confirmed the nano scale of multiple diazotized carbon black and it should be suitable for the naming "liquid" nano carbon (LNC).



(a) (b)

Figure 3. SEM image of Diazo 1 (a) and Diazo 4 (b) Magnification X 50,000

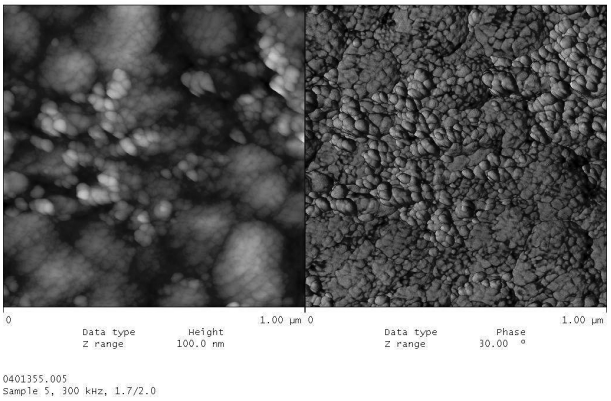


Figure 4. AFM image of dried film of Diazo4 spun from aqueous solution containing no additives

Thin Film Forming Properties of "Liquid" Nano Carbon

Generally speaking, thin film is determined by a thickness below 1um.The film having thickness greater than 1um belongs to thick film.Thin film is usually prepared by vacuum technologies including vacuum evaporator, sputtering, CVD, MBE. The thick film is only obtainable with solvent coating system with and without polymeric binder. In our approach, we are challenging a novel thin film coating with solvent using nano scale particles and no polymeric additives to achieve good film forming properties; i.e. no pin hole, good adhesion, thickness below 1um. The thin film forming properties of LNC on a Si wafer substrate require the wetness of coating solution against the inert surface of the Si, the adhesion against the substrate, the link between carbon particle in a two dimensional structure. As LNC is well stable in an aqueous media which normally beats up against Si surface, it is necessary to wet Si wafer surface with a third party. The Si wafer surface can be a polished and well cut (110), (100), (111) crystal, which all exhibits poor wetness against water. First, adhesion promoter such as AP 8000 (3- amino propyl triethoxysilane) from Dow Chemical shows significant improvement of adhesion of LNC layer on surface (110) of polished. Secondly, the wetness of (110) polished

Si surface can be significantly improved with a few drops of ionic surfactant such as Surfynol465 (Air Product). As above mentioned the nature of LNC, the nano scale carbon particles rebel each other in electrolytic environments such as strong polarizing water. Additives which can maximize the ionization of LNC tends to disaggregate more easily to form uniform solution for spin coating. Further, hydrophobic solvents can also help to separate nano scale particles better. Figure 6 is AFM image of a dried film of LNC spun from an aqueous solution of 5%wt LNC added with ionic surfactant Surfynol 465 (0.2% wt), 0.1%wt NaOH and 25% wt of IPA. The film was spun coated on a cleaned Si surface with spinning speed of 5000 rpm for 30sec. The spun film was dried at room temperature for several hrs. It is observed from this AFM image that all of carbon particles show the improved smoothness and uniformity without any pin holes on a (101) 400um thick polished Si wafer substrate. The thickness of the coated LNC film was detected to be about 400Ao by Nanometrics's thickness measurement tools (Nanometrics, Inc, California) based on optical reflection principle. It can be concluded that from the nano scale particle size determined by AFM techniques and from the thickness measurement determined by Nanometrics, that very nearly single layer of LNC was formed on Si wafer surface. No further electronic measurement for example, SEM or TEM, of the thickness was carried out at this point.

Micro Patterning Process of LNC on Wafer Substrate

The actual process of micro patterning of LNC is summarized in Fig. 7.

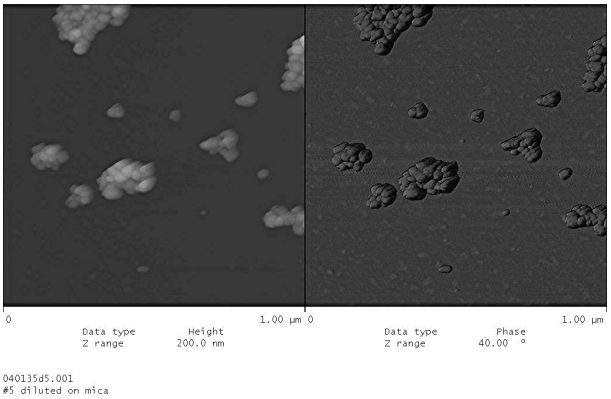


Figure 5. AFM image of Diazo4 flushed with a few drops of water

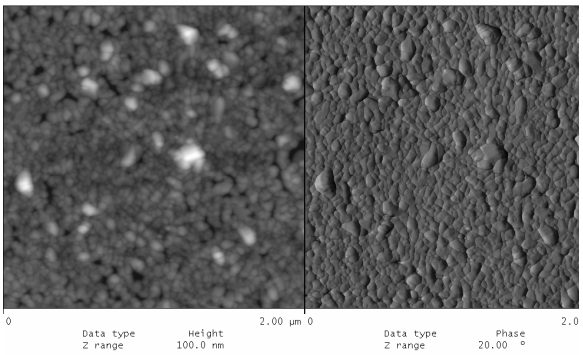


Figure 6. AFM image of LNC (Diazo4) thin film coasted from aqueous solution added with 0.2% surfynol 465 ,0. 1% of NaOH and 25% of IPA (all in wt%)

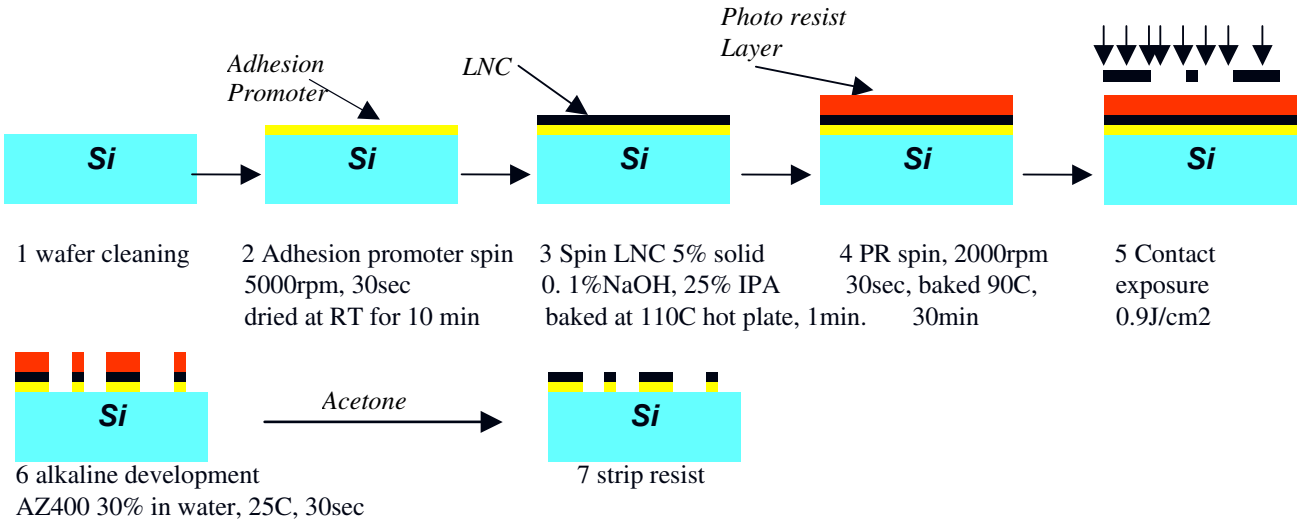
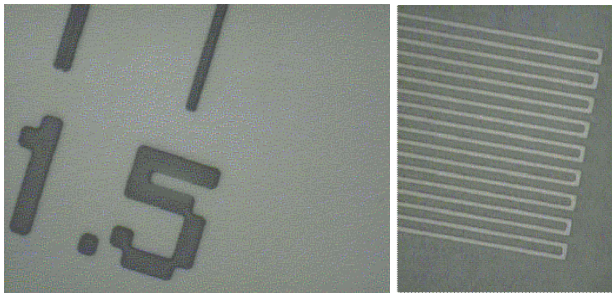


Figure 7. Describes the micro patterning process with LNC in the present study.

In this process, (101) single polished and cleaned 5” diameter Si wafer was inspected spin coated successively with adhesion promoter, LNC and positive photoresist. Figures 8(a) and 8(b) show the micro pattern image of LNC developed at the process end (step7). The development of image on LNC thin film can be explained by the solubility of LNC in alkaline developer: under exposure with UV light source, the positive resist becomes acidic and washed away with alkaline developer, the unexposed area protects LNC from alkaline attack. Development time, temperature, active components of developer should be major parameters to control the undercut of LNC layer. Figure 9 shows the micropatterns of negative resist formed on a transparent glass substrate. Without LNC coating (a) the micropattern image of the negative photoresist is not completely developed; i.e., the corner is not cleaned cut. Figure 9(b) exhibits the well developed image by using LNC as antireflection coating in the opposite site of the glass substrate.



(a) (b)

Figure 8. Micro patterns made out of LNC (a) (b) resolved 1.5 um line widths

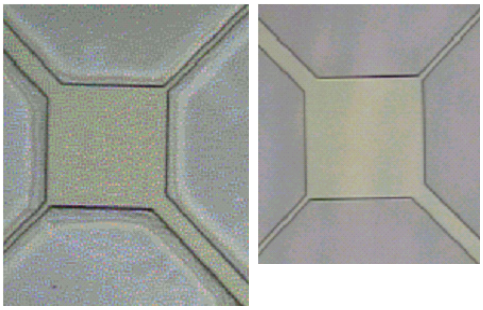


Figure 9. Fig.9 Developed image with LNC coating as anti reflection layer (a) W/o LNC coating (b) with LNC coating

Conclusions

It can be concluded from the present study that

a. Multiple diazotization of carbon black shows the effectiveness of the purification and maybe the increased concentration of electrolytic groups intentionally attached to it by diazo coupling reaction
b. As a result, the deaggregation due to electrostatic repulsive force in an electrolytic environment may cause further particle size reduction to nano scale and demonstrated the individual particle size in the range of 20-30nm.
c. The nano scale particles of carbon black demonstrated the capability of forming carbon thin film without using vacuum technology
d. Electrolytic groups on carbon surface helps to develop micropattern image based on the developed image of the positive photoresist
e. These processes are much more simple and much lower cost than the micropatterning process using plasma or thermal decomposition.
f. The above mentioned multiple diazotization process can be considered as a chemical top down process in nano scale fabricatiom, which is also more simple, lower cost compared to the conventional physical top down process

References

1. US Pat 5554739 and 5922118
2. Srikanth Ranganathan et al,Journal of The Electrochemical Society, 147 (1) 277-282 (2000)
3. US Pat 5,721,090

Author Biography

Yuan Yu, Friedrich Von Gottberg, IST2000, http://www.cabot-corp.com/cws/businesses.nsf/8969ddd26dc8427385256c2c004dad01/ffa05e513f25449385256c7a00502291/$FILE/SurfaceModification.pdf