

CARBONIZED NOVOLAC AND PVA STRUCTURES DEPOSITED ONTO Si SUBSTRATE FOR HIGH TEMPERATURE PHOTORESISTS

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Introduction

The fabrication of integrated circuits requires techniques that enable patterning of the various thin film materials used to build semiconductor devices at very high resolution. These techniques, the lithographic processes, involve the resist materials coating on the substrates and through a mask, the light strikes only selected areas. The exposed resist is then subjected to a developing step by the immersion in an appropriate solvent. Depending upon the chemical nature of the resist material, the exposed areas can become more soluble in the developing solvent which case a positive-tone image is formed, or they can become less soluble which case a negative tone image is formed [1]. Photoresist are traditionally polymeric materials, either single or multi-component systems [2]. Par example, the simplest are single component materials such as poly-methyl- methacrylate (PMMA), extensively used as resist in electron beam lithography. The patterned photoresist layer is used as protective mask for an etching process that selectively removes the undesired areas of the underlying film. So the used photoresist materials have a passive role regarding to the final device [3,4].

A reconsideration of classical polymer photoresists to be applicable with the new techniques- Deep UV, X-ray and e-beam lithography - is a very important target for circuit printing under 0.5 microns. The photoresist polymers are extensively used in micro and nanotechnology.

Electron beam lithography (EBL) is a specialized technique for creating extremely fine patterns, required by the modern electronics industry for integrated circuits. This method leads to very high resolution, almost to nano-metric level, versatile, that can work with a variety of materials and almost with an infinite number of patterns. Unfortunately is still expensive and complicated [5].

Like EBL, Ion beam lithography (IBL) exposes the patterned resist material to ion beams. The main advantage of ion beam lithography is the lack of a proximity effect, which causes problems with line width control in EBL. IBL offers the chance to dope the material if the proper ion species are used. This technique is not widely practiced because its technology is not as developed as the one for EBL. The disadvantages are related to the thickness of the resist that can be exposed and the ion bombardment damaging.

Optical lithography, used almost exclusively for all semiconductor integrated circuit manufacturing, reaches few tenths of microns in resolution. The deficiencies: overexposing / overdeveloping, phase shift phase edge masks and edge shadowing, require laborious processes thus being not suitable for complex devices [6,7].

X-ray proximity printing may be a useful lithographic technique for 0.25 μm or less features [8]. The disadvantage is that X-ray lithography is currently an extremely expensive alternative and the availability of good mask is limited. It also requires either a custom built X-ray source and stepper or access to a synchrotron storage ring to do the exposures. With care, X-ray lithography can also be extended to the less then 0.1 μm regime [9].

These new techniques claim also a reconsideration of the photoresist philosophy.

To design a resist material with these new techniques targeting very high resolutions requires a fundamental understanding of the chemical and physical processes that occurs in the thermal processes at the interface substrate-polymer resists, the interaction with plasma species.

The semiconductor class for high power circuits like SiC, GaN and heterostructures claims photoresists that will interact and give active components/species. The classical photoresists are used only for printing the pattern of the structure, so they have a passive role in the device development. An active photoresist will be that one which interacts with the surface under specific conditions and becomes an active component in the device structure. As example: the heterostructure Si-SiC-C, used in different types of high-power electronic devices.

This paper presents a new method to grow such active heterostructures starting with classical photoresist, in a proper way.

On silicon substrate, by spin-coating, a thin layer of photoresist is deposited. Depending on the photoresist, a thermal treatment between 200 - 300°C in argon atmosphere, is carried on. By specific methods the pattern is printed on the photoresist – UV exposure. (also X-ray, Ion-beam, EBL). The bright parts of the image pattern cause chemical reactions that make the resist material become soluble. After development, the resist forms a stenciled pattern across the wafer surface that accurately matches the desired pattern of a circuit. The final step in obtaining the heterostructure is the thermal treatment with a complementary plasma etching. Polymeric resist structure is altered and only the carbon structures remain intact. A higher temperature favors the interaction between the carbon and silicon. Silicon carbide forms at the carbon structure - silicon interface. This way a classical photoresist is converted into a Si-SiC-C (to 2-D graphene) heterostructure. The steps of this process are presented in fig 1 from (a) to (e).

Only the Si-SiC-C heterostructures formation, under thermal-plasma treatment is taken in account.

Experimental details

Novolac and PVA have been chosen for our studies.

The Novolac - HMTA (hexa-methylen-tetramine, catalyst) and ethyl alcohol solution is deposited on the silicon substrate by spin-coating. By a preliminary thermal treatment the deposited film is polymerized resulting a highly cross-linked structure. This means there is a large concentration of aromatic groups at the interface with the substrate. At this point the silicon is covered with a material very rich in carbon. The mismatch between aromatic rings and silicon is small, so a proper thermal treatment will lead to a SiC buffer mapping the silicon surface. To maintain the integrity of the future carbon structure the thermal treatment follows certain steps. The temperature is increased

with a slow rate up to 1200 °C in three steps: 1) 280⁰-polymerization process, fig.1a, 2) 700 °C -the elimination of hydrogen and other volatile groups like OH (10deg/hour), fig.1d, 3) 1200 °C - interface reaction and SiC growth (10deg/hour), fig.1e. SiC layer start to grow at interface at 700⁰C (fig.1d)

The top layer of carbon can be either removed or selectively doped becoming part of the final device.

PVA is deposited from an aqueous solution onto the silicon substrate by spin-coating and identically treated like novolac. Because the PVA has a filamentary structure it is expected to obtain cumulene and polyine structures. These poly-conjugated chains might be used as connecting wires between the active components in devices (a target for nanotechnology). The reactor for the thermal and plasma treatment has the configuration presented in fig.3.

The samples, characterized with Raman and XRD prove that the heterostructure Si-SiC-C can grow at a minimum temperature of 700⁰C(fig 2a, 2b)

Discussions

Raman spectra on PVA and Novolac exhibit several interesting features. The band, 620-1020cm⁻¹, (fig 2b - 1, 2) covers a large scattering from SiC [10-13]. The small amount in intensities is due the absorption in top layer of carbon. The Si substrate is well defined by the line 521cm⁻¹. Etching in Ar plasma destroys the SiC film and removes the amorphous carbon leaving only the well organized micro-domains (fig2b - 3). The amount of ordering, degree of sp² bonding and the domain size in the samples are quite different that in pyrolytic graphite (HOPG) and glassy carbon. The first order Raman spectra of HOPG is characterized by a single peak at 1580 cm⁻¹ (linewidth -15 cm⁻¹) corresponding to one of the two Raman active E_{2g} of the graphene sheet. The band appearing at 1350 cm⁻¹ is explained by the relaxation of the wavevector selection rules due the finite size of the crystals. Usually this band is specific for glassy carbon but can be a very good indicator of the domain size extent in 2D [14].

The sample Novolac700 has a high size effect (fig 2b - 2). The 1350 band is large shifted at 1314 cm⁻¹, also the peak at 1580 cm⁻¹ is shifted to 1595 cm⁻¹.The sample etched in Ar plasma (fig2b - 3) has a similar feature with the difference that SiC and carbon is partial removed (fig.4) keeping the initial pattern.

PVA does not show any degree of sp² bonding. XRD (fig2a) show a 2D-organizing by 100-line and SiC bonding to the Silicon substrate. Also the Novolac700 show an intense organizing with a strong 103-line.Both lines are shifted to smaller angles. The

lines (002) and (004) missed. These effects are the consequences of the spin-coating method (centrifugal and adhesion forces).

Conclusions

A new patterning method using active photoresists is proposed.

The spin-coating of the classical resist polymer with a subsequently thermal treatment gives the active structures with a preferential orientation. The initial pattern is kept during all stages.

At 700 °C at silicon substrate - carbon structure interface a reaction occurs. The XRD and Raman spectra show the formation of a thin SiC layer. The thickness of SiC layer can be adjusted by higher temperatures.

Pyrolysed polymers in interaction with substrate surface give a new class of ordered carbons with very high dimensionality character. Heterostructures Si-SiC-C are easily patterned.

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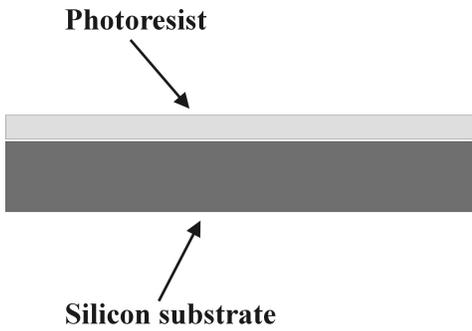


Fig.1a - The thermal treatment of the polymer resist deposited on the silicon substrate is carried on from 200 to 300⁰C in an inert atmosphere – argon.

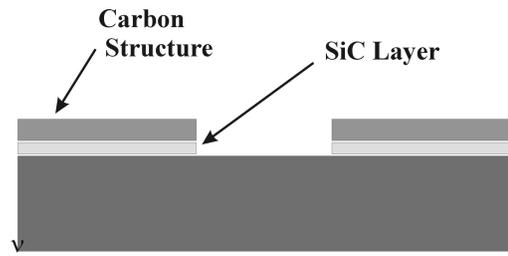


Fig.1d - The preliminary thermal treatment is carried out, in an inert atmosphere, up to 700-800⁰C for the elimination of hydrogen and other volatile groups.

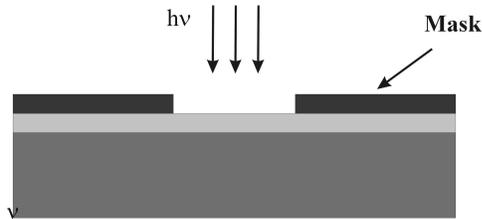


Fig.1b - By specific methods the pattern is printed on the photoresist – UV exposure, X-ray, Ion-beam, EBL.

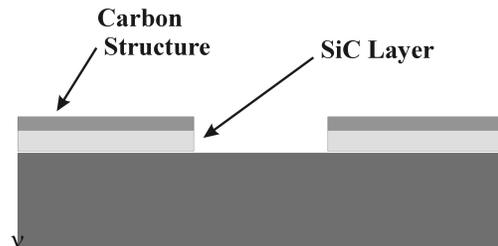


Fig. 1e- The high temperature-up to 1200⁰C- favors the interaction between the carbon and silicon with the formation of silicon carbide at the carbon chains and silicon interface

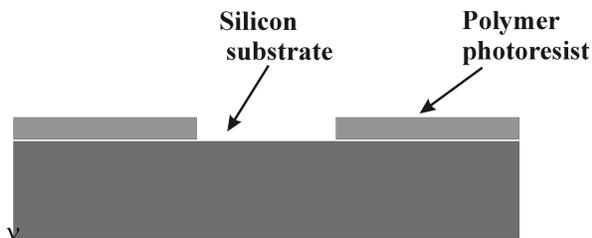


Fig.1c - After development, the resist forms a stenciled pattern across the wafer surface that accurately matches the desired pattern of a circuit.

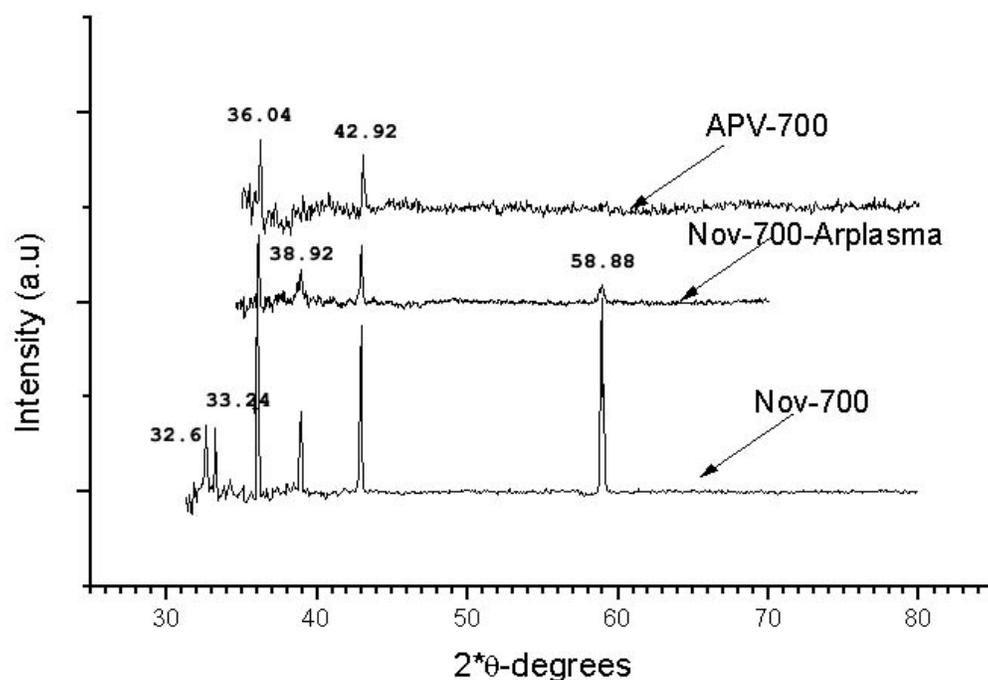


Figure 2a- XRD for: polyvinyl alcohol APV-700 , Novolac/HMTA (photoresist) -700 , Novolac/HMTA -700 treated in Ar-plasma; HMTA-hexamethylenetetramine (36.04- 111- β SiC; 42.92- 100 graphite; 58.88- 103 graphite)

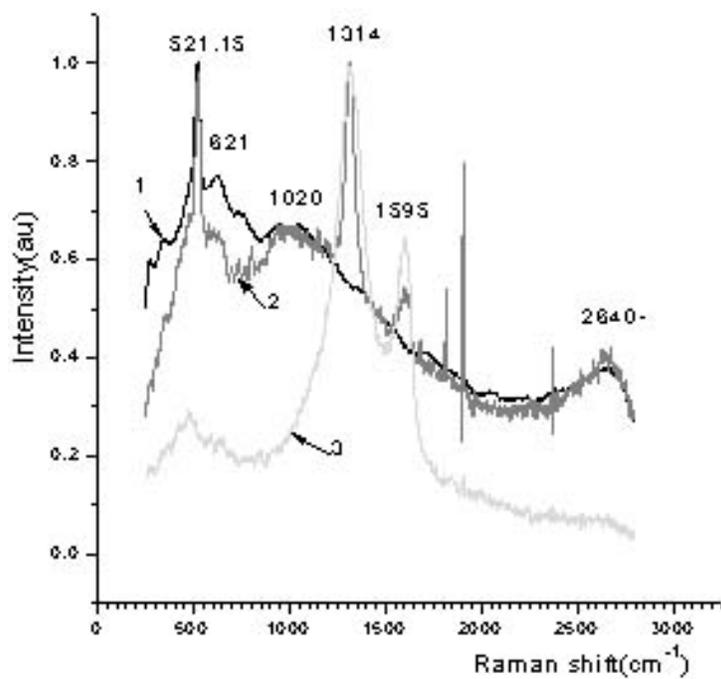


Figure 2b - Raman spectra for: polyvinyl alcohol APV-700 (1), Novolac/HMTA (photoresist) -700 (2), Novolac/HMTA -700 treated in Ar-plasma (3); HMTA-hexamethyltetramine

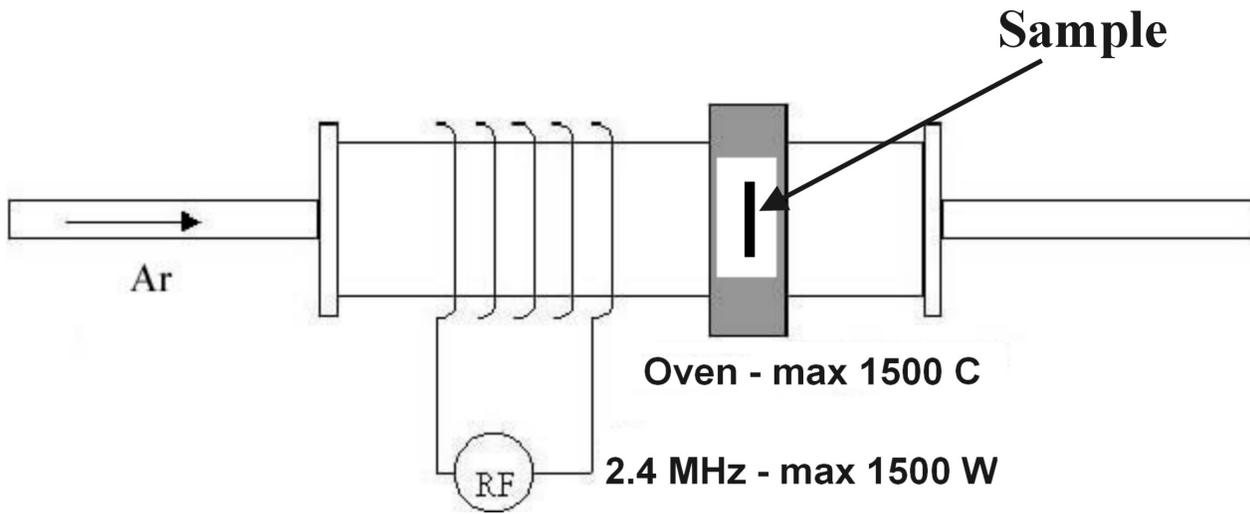


Figure 3 - The configuration of the reactor for the thermal and plasma treatment

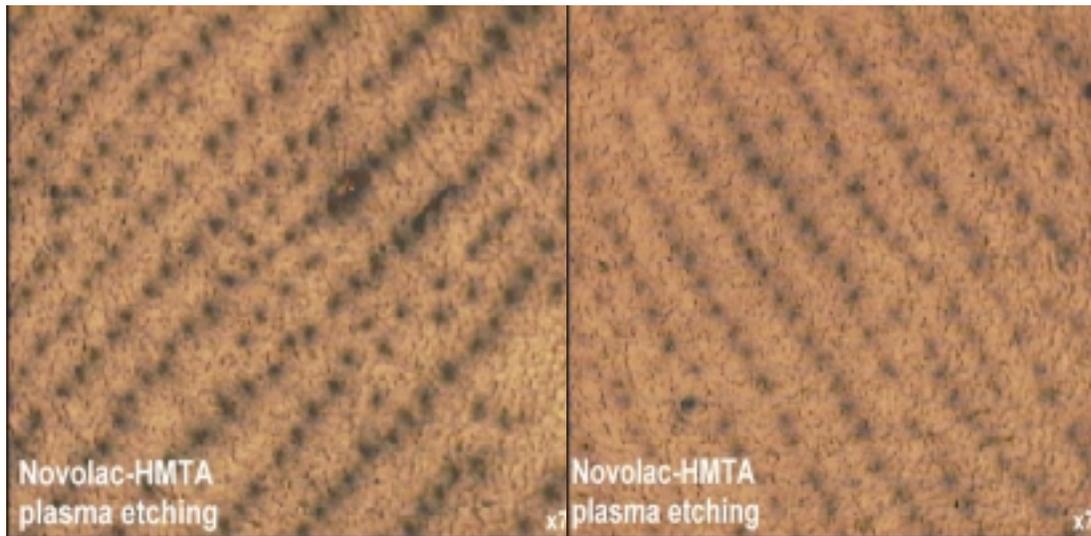


Figure 4 - The pattern of Novolac/HMTA-700⁰ C after Ar-plasma etching