

SYNTHESIS OF A FUNCTIONALLY GRADED PAD FOR CHEMICAL MECHANICAL PLANARIZATION

[0001] This claims the benefit under 35 U.S.C. 119 of

a) U.S. Provisional Application No. 60/475,305, entitled MODULATION OF POLISH PAD PROPERTIES THROUGH A RAMIFIED ALKYL AND ARYL FUNCTIONAL GROUP OF PRECURSORS, filed June 3, 2003, (57718-30003.00);

b) U.S. Provisional Application No. 60/475,374, entitled SYNTHESIS OF A GRADED PAD STRUCTURE FOR CHEMICAL-MECHANICAL PLANARIZATION USING REACTIVE INJECTION MOLDING, filed June 3, 2003, (57718-30004.00);

c) U.S. Provisional Application No. 60/475,283, entitled REINFORCED CHIP-CUSTOMIZED PADS FOR CHEMICAL-MECHANICAL PLANARIZATION PROCESSES, filed June 3, 2003, (57718-30005.00); and

d) U.S. Provisional Application No. 60/475,307, entitled INCORPORATION OF MULTI-FUNCTIONAL CURATIVE AGENTS IN PADS USED FOR A CHEMICAL-MECHANICAL PLANARIZATION PROCESS, filed June 3, 2003, (57718-30006.00), the entire contents of which are incorporated herein by reference.

FIELD

[0002] We describe polishing pads suitable for the chemical mechanical planarization (CMP) of semiconductor wafers. In particular, our description relates to polishing pads synthesized to give spatial grading in material/tribological properties. These differential gradings may be used to achieve custom polishing of various dielectric and metal films during silicon integrated circuit (IC) processing.

BACKGROUND

[0003] Chemical mechanical planarization (CMP) is used to planarize individual layers (dielectric or metal layers) during integrated circuit (IC) fabrication on a semiconductor wafer. CMP removes undesirable topographical features of the IC on the wafer, such as metal deposits subsequent to damascene processes. CMP may be used to remove excess oxide produced

during shallow trench isolation steps and to planarize inter-level dielectrics (ILD) & inter-metal dielectrics (IMD) including those having low-dielectric constant (low-k) materials.

[0004] CMP typically uses the combination of a reactive liquid medium and a polishing pad surface to provide the mechanical and chemical control appropriate in achieving planarity.

Either or both of the reactive liquid and the polishing surface of the pad may contain inorganic particles, often nano-size in dimension, to enhance the chemical reactivity and/or mechanical activity of the CMP process upon the wafer. The pads in common use today are often made up of a substantially rigid, micro-porous polyurethane material selected to achieve the simultaneous functions of providing uniform slurry transport, of providing for the distribution and removal of the resulting particulate products, and of providing uniform distribution of applied pressure across the wafer.

[0005] In a CMP process, the chemical interaction of the slurry fluid with the wafer results in the formation of a chemically modified layer at the polishing surface. Simultaneously, the abrasives in the slurry mechanically interact with the chemically-modified surface layers thereby resulting in material removal. The abrasive particles generally participate by a mechanical abrasion in the step of material removal. When viewed at the nanoscale level, the kinetics of the formation of and the subsequent removal of the thin surface layer, control the CMP output, that is to say, the removal rate (RR), the surface planarity, the surface defectivity, and the slurry selectivity. Therefore, the pad local material/tribological/mechanical properties are important to both local and global planarization during a CMP process.

[0006] The material removal rate (RR) in a CMP process is a function of a number of factors, but particularly is a function of the slurry abrasive concentration and of the average coefficient of friction ("f") in the pad/slurry/wafer interfacial region. The extent of normal and shear forces during CMP and the 'real-time f' depends both on the pad tribology and on the slurry rheology. Recent studies (ref. 1&2) indicate that the compliance of pad material, the area of contact between wafer and the slurry abrasive particles, and the extent of lubricity of the system all play significant roles during any CMP process.

[0007] As a way of quantifying the role of these factors in a CMP process, a Stribeck curve may be employed. By way of background, the Stribeck-curve is a plot of the average coefficient of friction "f" vs. Sommerfeld number, So [$So = \mu V / p \cdot d_{eff}$] and shows the extent of contact

amongst the wafer, the rotating pad, and the encased abrasive particles. (where μ = slurry viscosity, V = the relative pad-wafer velocity and $d_{\text{eff}} = \alpha \cdot R_a + [1 - \alpha] \cdot d_{\text{groove}}$, where R_a is the average pad roughness, d_{groove} is the pad groove depth, and ' α ' (dimensionless area parameter to scale the wafer pressure) = $A_{\text{up-features}}/A_{\text{flat pad}}$; $p_{\text{eff}} = p/\alpha$

[0008] The generic Stribeck-curve provided in Figure 1 depicts three distinct regimes: a "boundary lubrication regime," a "transition regime," and a "hydrodynamic lubrication regime." First, in the 'boundary lubrication regime,' all solid bodies are in intimate contact with slurry abrasive particles and ' f ' remains constant with S_o . In this regime, larger values of ' f ' and 'RR' occur.

[0009] Secondly, at intermediate ' S_o ' values or in a "partial lubrication regime" or "transition region regime," the pad and the wafer are not in direct contact due to the presence of a fluid film layer or perhaps due in part to the roughness of the pad. In this transition regime, the slope of ' f ' is negative.

[0010] Finally, in the "hydrodynamic lubrication" regime or at the at larger values of S_o , the presence of a thicker fluid layer results in smaller 'RR' and ' f ' values. Any slight increase in ' f ' with increasing S_o would likely be due to the occurrence of eddies in the fluid flow field ($f = k \cdot S_o^\beta$, where k is a constant and β is the tribological mechanism indicator of the lubrication regime). For $\beta > 0$, the boundary lubrication mechanism dominates. For negative values of β , the partial lubrication regime is in evidence and a lower RR ($RR = K_{Pr} \cdot p_{\text{eff}} \cdot V$, where K_{Pr} is the Preston's constant that depends on the chemo-mechanical aspects of the process).

[0011] The partial lubrication regime (or transition region regime) offers increased pad life. However, operation in the boundary lubrication regime offers greater stability, control, and predictability in RR and wafer uniformity. Both ' f ' & ' β ' have a linear relation with K_{Pr} and hence with RR. K_{Pr} is inversely proportional to the pad storage modulus. Thus softer pads with higher compressibility provide larger RR and harder pads with lower compressibility provide lower RR. A softer pad experiences a greater shear force at the leading edge of the wafer during polish since it is comparatively more compressed and thus creates a barrier that the wafer must continuously overcome during the wafer's motion. On a micro-scale, the pad asperities at the wafer/pad interface are collapsed thereby increasing the shear force, components of both f and β .

[0012] The compliance, microtribology, and nanotribology of the pad material along with the slurry rheology, variously, the lubricity, the configuration of grooving or perforations, the abrasive concentration, the pH, and the temperature each may alter the shape of a specific Stribeck curve, may alter the relative extent of different lubrication regimes, and the values of K_{Pr} , f and β .

[0013] The pads that we describe herein, may have differing regions of pad tribology. By modulating pad tribology and choosing appropriate operating regimes of Stribeck curve lubricity for those modulated or differing regions, simultaneous local and global planarization may be attained even for wafers having dissimilar material stacks (such as may be found in metal/barrier, oxide/nitride constructs as found in shallow trench isolation (STI)); or those having the materials plied for sub-90nm technologies (such as the low-k and strain-Si materials and silicon-on-insulator (SOI) constructs), and those having complex device design and architectures such as those evident in "system-on a-chip" (SoC) and various vertical gate structures (e.g., the FinFET). Our modulated or functionally graded pads may be designed for wafers having a wide range of varying pattern densities and chip sizes.

[0014] Conventional open-pore and closed-pore polymeric pads with substantially homogeneous tribological, chemical, and frictional characteristics have been suitable for use in CMP. The introduction of 250 nm CMOS technology, however, probed the limits of those pads' suitability. For sub-250 nm technology, for instance, technologies having increased complexities of design (e.g., SoC), process (e.g., SOI, FinFETs), or materials (e.g., Cu or low-k materials) particularly when coupled with substantial variations in chip pattern density and increased chip size, use of those conventional open-pore and closed-pore homogeneous polymeric pads has accompanied deterioration of chip yields, device performance, and device reliability as compared to the same measures in earlier generations of wafers.

[0015] Various attempts to change pad thickness (stacked and unstacked) and pad surface conformations (e.g., perforated, K-groove, X-Y groove, and K-groove/X-Y groove combinations) have not specifically addressed the impact that chip pattern density, chip size, complexity of architecture, and dielectric/metal process flow have on ultimate chip yield, device performance, and reliability of integrated circuits.

[0016] The functionally graded pads described here, having spatial variations of the pad tribological/material properties, are suitable for CMP processes on these new technologies, even for those using sub-130nm technology nodes.

SUMMARY

[0017] Described is a functionally graded polishing pad for a CMP process made up of a polishing pad having a polishing surface for polishing a silicon-containing wafer that is configured for use in a CMP procedure, wherein the polishing surface is one piece, substantially flat, and comprises at least two areas having differing physical characteristics. The at least two areas may have discrete boundaries or boundaries that are formed of mixtures of constituent polymers. The at least two areas may each comprise a compositionally different polymeric material and the region between the areas may comprise mixtures of the compositionally different polymeric materials.

[0018] The shape of at least one of the at least two areas may be annular, an island, or of random shape. The at least two areas each comprise a different polymeric material having different physical parameters and the change in composition between the at least two areas may be a step change, a continuous change, or a combination. The pad may have an edge and a center and the edge comprises one area and the center comprises another area and the change in composition between the edge and the center may be continuous or step or another form.

[0019] The functionally graded polishing pad may be made by the process of sequential or simultaneous injection molding of at least two polymeric compositions to form said at least two areas. The functionally graded polishing pad may have at least one of the at least two polymeric compositions comprising a block copolymer, perhaps where the block copolymer has differing constituent polymeric composition in the block copolymer over distance.

[0020] In a graded pad, the key pad mechanical properties like hardness, modulus amongst other and physical properties like porosity are varied spatially. Several types of grading can be conceived of which include patterns that can be classified as annular grading, island grading and step grading. Many other grading patterns are possible depending on the type of operation. The most appropriate pad grading for a particular operation is developed using simulation methods based on parameters which include the wafer sweep and its residence time distribution during CMP, coefficient of friction and other physical properties.

BRIEF DESCRIPTION OF THE DRAWINGS

- [0021] Fig. 1 depicts an exemplary generic Stribeck curve indicating the extent of contact between the rotating wafer, the rotating pad, and the encased abrasive particles in various lubrication regimes.
- [0022] Fig. 2 depicts a schematic one-shot technique for producing graded polishing pads where isocyanate, polyamines/polyols, chain extenders, and other additives are all blended together.
- [0023] Fig. 3 depicts a schematic prepolymer or "two-shot" technique for producing graded polishing pads.
- [0024] Fig. 4 depicts a schematic step-graded pad having an outer ring of one formulation and an inner region of a second formulation having different tribological properties.
- [0025] Fig. 5 depicts a step-graded pad having islands of one polymeric formulation and a surrounding region of a polymeric matrix having a different tribology.
- [0026] Fig. 6 depicts a graded pad having a complex grading with varying shapes, sizes, and materials with tribological properties.
- [0027] Fig. 7 shows a continuously graded pad where the center comprises a first formulation at the center and the edge comprises a second formulation.. In this variation, the two formulations are completely miscible.
- [0028] Fig. 8 shows a graded pad where the grading is a micro-domain morphological texture using injection of a block or grafted copolymer.
- [0029] Fig. 9 depicts schematically a phase diagram (Temperature – Composition) of block copolymers with different equilibrium structures (bcc, hcp and lamellae).

DETAILED DESCRIPTION

Functionally Graded Polishing Pads

[0030] Described below are polishing pads suitable for use in the CMP procedure for polishing silicon-containing wafers mentioned above. These pads having at least two areas on the polishing surface adjacent the polished silicon wafer, having differing material characteristics. The areas may be discrete and well-defined with clear borders. The areas may be of a type wherein the material characteristics vary over a distance. Our polishing pads comprise one or more polymeric materials that each may comprise one or more of the following:

neat polymers having a specific molecular weight or molecular weight distribution, mixtures or alloys of one or more polymers, co-polymers of two or more species, and block co-polymers of two or more species. The polymeric composition may be filled with other polymeric or non-polymeric materials, e.g., polymeric fibers, natural fibers, particulate materials such as discrete "crumbs" of polymeric materials, etc.

[0031] The surface of our described polishing pad adjacent the polished wafer surface may be substantially flat after completion of the synthesis steps described here. Grooved and hilled surfaces having the characteristics noted here.

[0032] Materials suitable for the described CMD polishing pads include a wide variety of polymers, including such diverse polymers as: polyurethane, polyurea, polycarbonate, the Nylons, various other polyesters, polysulfone, various polyacetals, and the like. These polymeric material and their chemically related brethren and may be used for the fabrication of the CMP pad. Other polymer chemistries may, of course, be used. Formulations of using these materials necessarily involve some understanding of the relationships between the structure of the polymeric material and the resulting physical properties. The processing characteristics of the various constituent and composite materials, e.g., inter polymer compatibility between various areas, reactivity, and viscosity.

[0033] One polymer system having a significant scientific, engineering, and commercial history is the polyurethane and polyurea chemistry system. These polymer products often comprise isocyanates, polyols, polyamines, chain extenders, etc. Commercially speaking, more than 90% of isocyanates are toluene-diisocyanate (TDI) or diphenylmethane-diisocyanate (MDI) and its derivatives. Others include polymethylene polyphenyl isocyanate (PAPI). Isocyanate functionality is important as it leads to crosslinking and therefore hardness as well as other pad compliances. The size and molecular weight of the polyamines/polyols reactants contribute to the flexibility, low temperature properties, hydrophilicity, light stability and processing characteristics of the resulting polymer.

[0034] Chain extenders are often low molecular weight diamines or diols used to increase urea/urethane content in the final polymer. They react with the isocyanate and become part of the "hard segment" in the resultant polymer and often substantially influence the hardness as well as the elastic compliance. Many available chain extenders will also modify process

characteristics such as gel time and viscosity build-up. The strength of the ultimate product is also often affected. Crosslinkers are characterized by molecular weight and functionality. Low molecular weight molecules are effective at crosslinking the polymer matrix on a molar basis and effect increased resistance to swelling, low temperature flexibility, and processing kinetics.

[0035] There are two well-known approaches for formulating polyurea/polyurethanes. They are known as: (i) "one shot" technique, and the (ii) "two shot" technique. Figure 2 shows a schematic of the one shot technique. In summary, the components (e.g., a long chain diol, a diisocyanate, and, as needed, a chain extender) are mixed and reacted together. However, such a process is difficult to control. Local concentrations of reactants in the reaction mixture and random thermal control sometimes result in widely varying polymer product characteristics.

[0036] Figure 3 shows a schematic depiction of the two shot technique. The isocyanate is pre-reacted in a first step with the long chain diamine/diol to form a high molecular weight isocyanate, typically known as the "prepolymer." This functionalized prepolymer is then further reacted with diamine/diol curatives or chain extenders to complete the polyurea/polyurethane formation. This process is more easily controlled but requires higher processing temperatures often in the neighborhood of 100°C.

[0037] It should be apparent that our polishing pads may comprise a neat polymer such as the polyurethane or polyurea materials discussed just above or may comprise two or more different molecular weight product polyurethanes or polyureas materials in the different areas on the polishing surface.

[0038] This explanation of a pair of methods for producing polyurethane or polyurea materials should be viewed both as an example of producing those polymers and as an example for placing other polymers in the synthesis of graded pads. Such an example should not be considered as a limitation on the scope of the disclosure.

Multiple Injection Molding

[0039] Another variation of the process for making functionally graded pads comprises a process known as multiple point injection molding (also called coinjection sandwich molding). Multiple injection molding is a sequential process in which two or more polymeric materials are

utilized, however each of the materials is injected into the mold at a different time. This process is different from the in situ multiple injection molding process described below.

[0040] An example of a procedure for synthesizing a two-area graded pad where two different polymeric compositions are used, one for each area, is this. As shown in Figure 4, a first outer annular ring of the pad is molded using an injection molding process. The completed outer ring is then placed in a second mold and the center of the pad ring is then filled with a second polymeric material. Said again: in the first and second molding steps, two different materials are used so that in the resulting pad which has two distinct regions or areas of different (mechanical and physical) properties. Proper bonding at the interface between the two materials may require selection of materials that are compatible with each other. Such information is readily available in the open literature. Interfacial compatibility between two polymers is usually good.

[0041] This method may be used to form graded pads with more than two areas and with more than two steps. Further, this method may be used to achieve any step grading pattern from the simplest, most well defined annular patterns to the most complex and random of patterns.

[0042] Figures 5 and 6 show more complex patterns as may be made using this process. The crosses shown in Figure 5 (as region 2) are fenced by cross shaped forms or dividers so that neither polymer invades the other's space. The cross-shaped molds or forms are removed from the partially molded pad after the one or the other of the regions is filled.

[0043] Figure 6 shows a non-regular set of patterns defining, on a CMD polishing pad (200), a variety of chosen areas: ovals (202, 203, 204) and flag (205). In each of the noted areas, the respective polymers may each be a different polymer of the types discussed above or at least two differing ones. Again, such patterns may be achieved by using appropriate mold geometries.

Multiple live-feed (or in situ) injection molding

[0044] Molds including multiple in-situ injection ports may be used to make a graded pad. In this method a mold is selected at least two ports, generally independent, for injection of polymer. At least two different polymers are injected through the ports during the same injection step, often at the same time, to fill the mold. Depending on the grading requirements needed for the pad, the usual polymer engineering calculations may be used to calculate the fluid flow and heat

transfer needed for selection of appropriate injection points and of injection flow rates for the different polymers being fed into the mold.

[0045] Figure 7 shows a continuously graded polymer pad (210) made using this process by injecting a first polymer from the outer periphery (212) of a mold while simultaneously injecting a second polymeric material from the center.

Block copolymers

[0046] A block copolymer system may be used to produce a graded pad. Figure 8 shows a phase diagram portraying, in a functional way, the relationship between the block copolymer composition (as the relative % constituents) and the crystal structure (BCC, HCP, etc.) of the final product. To attain a gradation in properties, the composition of the block copolymer is gradually. Hence, in a controlled fashion, the difference in geometry is achieved in the block copolymer by spatial variance. Because the geometry and the % of (A or B) is changing spatially, as well as the fact that A and B are different units - the variance provides a gradation in physical properties such as hardness, modulus, porosity (by solution removal of A or B), roughness, and asperity

[0047] Specifically, hardness gradations may be achieved by varying the concentration of the molecular units of the block copolymer over distance since the two molecular units A and B used to make the pad will be of different hardness values. Furthermore, the variation in crystal structure produced as a result of the compositional relationship shown in Figure 9 creates additional and controllable variations in physical parameters.

[0048] Molecular units suitable for these procedures involving block copolymers include such materials as styrene, isoprene, butadiene, urethanes/urea, long-chain diols and diamines, etc.

Gas assisted injection molding

[0049] A method to produce a graded pad having included microporosity would be to include a gas during the injection molding step to achieve functional grading of porosity in the polymer polishing pad. Gas may be dispersed into and injected into the mold from different

ports with different flow rates in order to attain grading. The resulting pad will contain differing amounts of included gas at differing points and achieve a difference in hardness or density.

Reaction injection molding (RIM)

[0050] Particular polymeric systems (e.g., polyurethanes) are amenable to molding steps using the RIM techniques. In this molding process, instead of injecting previously synthesized polymers, the constituent monomeric materials and appropriate crosslinking agents (e.g., glycerol) as well as the initiating agents and chain extenders are added and the resulting mixture is polymerized while molding. To make a graded pad, multiple ports are used to inject two or more types of monomeric units (and corresponding chain extenders) to achieve gradation in chemical structure. Gradation in chemical structure will result in gradation of the mechanical and physical properties.

[0051] By differentially adding the monomers to the mold, this method may be used to produce step graded pads as well as the continuous pads discussed above.

Lamellar injection molding

[0052] By using mixtures of polymers that have been previously extruded, perhaps in layers, in an injection molding procedure such as those discussed above, polishing pads having the graded characteristics may be produced. This way of producing simple physical mixtures of polymers is direct and easily applied to changing demands upon a producer. The resulting gradation of properties will be according to the mechanical and physical characteristics of the individual polymers.

[0053] This method can lead to microdomain gradation.

Microcellular (Mucell molding)

[0054] In this technique the polymer fluid being molded is mixed with gas in order to form a solution mixture. Utilizing two or more such solutions with different chemistries will lead to a gradation of both the mechanical properties and the porosity.

[0055] The goal of using a graded pad for a CMP process is to allow different regions of the wafer being polished to be exposed to different chosen regions of the polymer pad in a selected manner. For example: it may be beneficial for the outer perimeter of the wafer to be exposed to the softer regions of the pad where the frictional shear force is higher than the harder regions of the pad; in comparison it may be beneficial for the inner regions of the wafer to be exposed to the harder regions of the pad to achieve a higher planarization length. Since both the wafer and the pad are in motion (rotation, oscillation) during any CMP process using these graded polymer pads in conjunction with residence time distribution models would achieve simultaneous local and global planarization. The material removal rate, defectivity, erosion, and dishing of the wafer and the effective planarization length of a CMP process depends upon the local tribology [hardness, compliances] and physical properties [pore size & density, asperities] of the pad material. Our functionally graded polishing pads permit choice of the local and global physical pad parameters allowing improvement of these CMP shortcomings.

CLAIMS:

1. A functionally graded polishing pad for a CMP process comprising a polishing pad having a polishing surface for polishing a silicon-containing wafer and configured for use in a CMP procedure, wherein the polishing surface is one piece, substantially flat, and comprises at least two different areas having differing physical characteristics, and wherein the different areas comprise two or more different molecular weight polyurethanes.
2. The functionally graded polishing pad of claim 1 wherein the polishing pad further comprises polyurea.
3. The functionally graded polishing pad of claim 1 or claim 2 wherein the polishing pad further comprises a chain extender.
4. The functionally graded polishing pad of claim 3 comprising poly(urethane-urea) that is made by a process wherein the isocyanate is reacted with long chain diol and diamine to form a prepolymer that is subsequently reacted with diamine/diol curatives or chain extender to form the poly(urethane-urea).
5. The functionally graded polishing pad of any of claims 1-4 wherein at least one of the at least two areas comprises a block copolymer comprising said polyurethane.
6. The functionally graded polishing pad of claim 5 wherein the at least two areas each comprise a compositionally different polymeric material.
7. The functionally graded polishing pad of claim 6 wherein the at least two areas each comprise a different polymeric material having different physical parameters and wherein a region between the areas comprises mixtures of the compositionally different polymeric materials.
8. The functionally graded polishing pad of any of claims 5-7 wherein at least one of the at least two areas is annular.
9. The functionally graded polishing pad of any of claims 5-8 wherein the at least two areas each comprise a different polymeric material having different physical parameters and wherein the change in composition between the at least two areas is a step change.

10. The functionally graded polishing pad of any of claims 5-8 wherein the at least two areas each comprise a different polymeric material having different physical parameters and wherein the change in composition between the at least two areas is a continuous change.

11. The functionally graded polishing pad of any of claims 1-10 wherein the at least two areas each comprise a different polymeric material having different physical parameters and wherein the pad is circular with an edge and a center and the edge comprises one area and the center comprises another area and wherein the change in composition between the edge and the center is a continuous change.

12. The functionally graded polishing pad of any claim above produced by the process of sequential injection molding of at least two polymeric compositions to form said at least two areas.

13. The functionally graded polishing pad of any of claims 1-11 produced by the process of simultaneous injection molding of at least two polymeric compositions to form said at least two areas.

14. The functionally graded polishing pad of any claim above wherein at least one of the at least two polymeric compositions comprises a block copolymer having differing constituent polymeric composition in the block copolymer over distance.

15. The functionally graded polishing pad of any claim above wherein the graded pad has hardness gradations.

16. The functionally graded polishing pad of claim 15 where in the hardness gradations result from varying the concentration of molecular units of a block copolymer over distance.

17. A method of making a functionally graded polishing pad for a CMP process having a one-piece polishing surface comprising forming the pad by injecting two or more polymeric materials into a mold at different times.

18. The method of claim 17 wherein at least one of the polymeric materials is formed by first reacting an isocyanate with a long chain diol to form a high molecular weight isocyanate

prepolymer, and reacting the isocyanate prepolymer with diol curative or chain extender to form a polymer suitable for CMP.

19. The method of claim 17 wherein at least one of the polymeric materials is formed by first reacting an isocyanate with long chain diamine and diol to form a high molecular weight isocyanate prepolymer, and reacting with diamine and/or diol curatives or chain extenders to form a polymer suitable for CMP.

20. The method of claim 18 or claim 19 wherein the isocyanate comprises a block copolymer.

21. The method of claim 20 wherein the block copolymer has different constituent polymeric composition over distance.

22. The method of claim 20 wherein the concentration of the molecular units of the block copolymer of the pad varies over distance.

23. The method of claim 22 wherein the variation in concentration of the molecular units of the block copolymer over distance provides hardness gradations in the pad.