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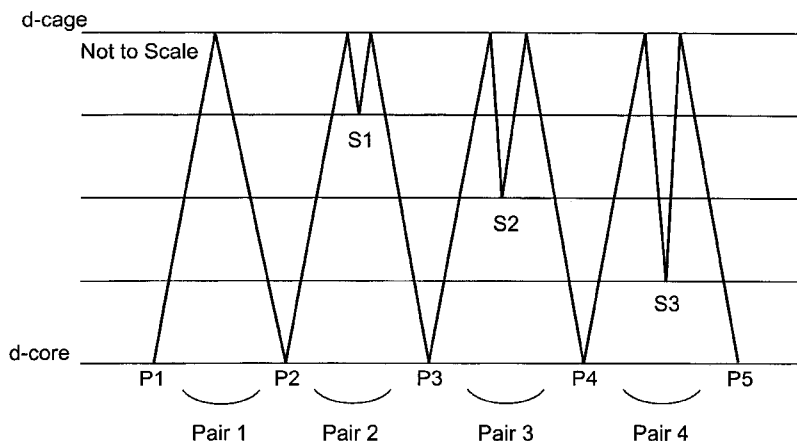


Figure 4

(57) Abstract: Versions of the invention include a pleated filter with a repeating pattern of primary and at least two types of secondary pleats. The repeating pattern of primary and the secondary pleats has improved resistance to flow deterioration or flow loss compared to traditional M-pleated filters with only a single type of secondary pleat.

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FILTER PLEAT STRUCTURE

This application claims the benefit of U.S. Provisional Application No.: 61/218,730 filed June 19, 2009 the contents of this application incorporated by reference in its entirety into the present application.

BACKGROUND

Cleaning baths used in the semiconductor industry can contain corrosive and oxidizing chemicals. Some of these cleaning baths can outgas and can produce gases and bubbles. One example of such a cleaning bath is an SPM bath. SPM bath solutions contain $(\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2/\text{H}_2\text{O})$ and are used to remove metal ions and organic substances from wafers. Filtration of these cleaning baths utilizes filters with porous membranes of inert materials like PTFE and the like. During use in cleaning baths where gases are evolved, dewetting of the filter membrane can occur and in some cases a deterioration of the flow rate of bath chemicals through the filter can occur. This can lead to reduced cleaning efficiency of the bath.

Pleated filters having various pleat patterns have been disclosed that include large primary pleats (P) and one or more secondary pleats (S). For example, U.S. Pat. Application Publication No. 20050045553 discloses a repeating pattern of pleats primary pleats P and secondary pleats S1 and S2, in the pattern P, S1, S2... with height ratios of P, S1, and S2 in a ratio of for example 3:2:1. Wicks, U.S. Pat. No. 2,627,350, discloses repeating patterns of primary and secondary pleats such as P, S1, S2, S1...(see FIG. 3 of U.S. Pat. No. 2,627,350 where $S1 < S2$); P, S1...(see FIG. 5 of U.S. Pat. No. 2,627,350); P, S1, S2...(see FIG. 6 of U.S. Pat. No. 2,627,350, where $S1 < S2$). Japanese Patent JP-11347329 discloses repetitive pleat pattern P, P, S1, S2...(see FIG. 1 of Japanese Patent JP-11347329 where $S1 < S2$). JP 64-17307 discloses a repetitive pleat pattern P, P, P, P, S1, S2, S1...(see FIG. 4 of JP 64-17307, where $S1 < S2$); JP 64-17307 discloses repetitive pleat pattern P, S1, S2...(see FIG. 2 of JP 64-17307 where $S1 < S2$). Japanese Utility Patent No. H02-70706 discloses repetitive pleat pattern as shown in FIG. 6 of the present application. In FIG. 6, the repetitive pleat pattern P, P, P, P, P, S2, S1, S3... shows that pleat 4a is a secondary pleat and is not a primary pleat 4. Further, as can be seen in the inset (B) of FIG. 6, pleat 4a does not touch core labeled with reference number 5: $S3 > S2 > S1$).

U.S. Pat. No. 6,315,130 to Olsen, describes problems associated with repetitive and uniform pleat patterns that result from short pleats of the same height that arise at a uniform frequency. One problem identified by Olsen for repetitive pleat patterns is migration of shortened pleats and less than optimum pleat density. Olsen discloses a non-repetitive pleat arrangement or a distribution of primary and secondary pleats, the heights of the secondary pleats are calculated so that all the secondary pleats have a different height. In some cases for practical reasons (pleater operation, ability to fit filter pack within cage), some secondary pleats have the same minimum height or are omitted from the filter pack.

There continues to be a need to reduce flow rate deterioration of pleated filters, especially in corrosive and gas generation environments such as cleaning baths or chemical compositions used in manufacturing environments.

SUMMARY AND DESCRIPTION

While various compositions and methods are described, it is to be understood that this invention is not limited to the particular molecules, compositions, methodologies or protocols described, as these may vary. It is also to be understood that the terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope of the present invention which will be limited only by the appended claims.

It must also be noted that as used herein and in the appended claims, the singular forms "a", "an", and "the" include plural reference unless the context clearly dictates otherwise. Thus, for example, reference to a "pleat" is a reference to one or more pleats and equivalents thereof known to those skilled in the art, and so forth. Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art. Methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the present invention. All publications mentioned herein are incorporated by reference. Nothing herein is to be construed as an admission that the invention is not entitled to antedate such disclosure by virtue of prior invention. "Optional" or "optionally" means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where the event occurs and instances where it does not. All numeric values are herein can be modified by the term "about" or "substantially" whether or not explicitly indicated. The term "about" or "substantially" generally refers to a range of numbers that one of skill in the art

would consider equivalent to the recited value (i.e., having the same function or result). In some embodiments the term "about" or "substantially" refers to $\pm 10\%$ of the stated value, in other embodiments the term "about" or "substantially" refers to $\pm 2\%$ of the stated value.

While compositions and methods are described in terms of "comprising" various components or steps (interpreted as meaning "including, but not limited to"), the compositions and methods can also "consist essentially of" or "consist of" the various components and steps, such terminology should be interpreted as defining essentially closed-member groups.

To reduce deterioration of liquid flow through pleated filters in various filtration applications, a filter with an alternating repetitive pattern of one or more primary pleats separated by one or more secondary pleats of different heights, the secondary pleats are arranged in a repetitive pattern between the primary pleats, has been found to reduce the liquid flow deterioration in the filter as compared to filters with other repetitive pleat patterns based on nitrogen purge testing of wetted filters.

In various illustrations and figures of the specification, it is to be understood that although the tip of each pleat is illustrated as a point, giving the pleat a "V" shape, the tip actually may be slightly rounded as shown in some of the cited documents of record. The radius of the tip may be determined by the characteristics of the implement used to create the pleats in a sheet of filter material as well as the thickness of the filter material sheet. In versions of the invention, the pleat material may consist of multiple sheets. For example, the filter material sheet may be a porous, microporous, or nanoporous membrane that can be placed between one or more drainage layer sheets and or support layer sheets.

Compression Rate is measured in a thickness direction of the pleats in a circumferential direction of the filter. The compression rate is a measure of how far the pleats are compressed in a thickness direction.

The nitrogen purge treatment of pleated filter structures can be used to measure flow deterioration of different pleat structures. In this test the pre-wet filters are N_2 purged for the testing using the following procedure: after prewetting the filter membrane with IPA 60% by weight in water, nitrogen gas at a pressure at 6kg/cm^2 is applied to the membrane (released with atmosphere pressure). This cycle is 15 times repeated and then the filter is characterized for flow efficiency, for example using water, at flow rates as shown in FIG. 2 and FIG. 3.

FIG. 1 shows a repetitive pattern of pleats that can be used in a filter that includes a pleated microporous membrane. The pleat pattern can comprise, consisting essentially of, or consist of a repeating pattern of primary pleats and secondary pleats. The primary pleats have a height P measured between an inner core of the filter and an outer cage of the filter, a first

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secondary pleat that has a height S1 and a second secondary pleat that has a height S2; S1 is different from S2 and both S1 and S2 are less than P. The repeating pattern of primary pleats and secondary pleats can be represented by the notation (P, P, S1, P, S2...), where P represents the primary pleat, S1 and S2 represent the secondary pleats, and the notation "..."
5 indicates that the pattern repeats. For example 2 cycles of the pleat pattern in FIG. 1 would be represented by the notation P, P, S1, P, S2, P, P, S1, P, S2 and so on. As can be seen by the representation in FIG. 1, there is an alternating repetitive pattern of one or more primary pleats separated by one or more secondary pleats of different heights, the secondary pleats are arranged in a repetitive pattern between the primary pleats. In this version, a pair of primary
10 pleats P and P are separated from another single primary pleat P by a first secondary pleat S1 and this single primary pleat is separated from another pair (only a portion of one primary pleat is shown) of primary pleats P, and P by a second secondary pleat S2 that has a height different from the first secondary pleat.

When sample filters with the inventive pleat structure illustrated in FIG. 1 (these are
15 designated by reference numbers in the Table in FIG. 1 as 2008-229-1, 2008-229-2, 2008-229-3, 2008-229-4) were compared by accelerated nitrogen purge treatment or testing with a filter that had a "1/2M" pleat structure (see FIG. 5), the filters having the pleat structure of FIG. 1 showed little or no increase (in two cases even a decrease 2008-229-3 and 2008-229-4) in differential pressure across the filters after the nitrogen purge while the filter with the
20 standard filter N8M707134 with the "1/2M pleat structure showed a noticeable increase in differential pressure (0.21 kg/psi (prewet) to about 0.26 kg/psi (after nitrogen purge)).

Flux ratio testing of these same filters after nitrogen purge treatment is shown in FIG. 3 at various flow rates. The standard filter N8M707134 with the "1/2M pleat structure clearly showed a decrease from about 6 (L/min/m² ΔP) to less than 5 (L/min/m² ΔP), a
25 decrease of at least 16 percent in efficiency, while samples using a version of the pleat structure of the invention, 2008-229-2, 2008-229-3, 2008-229-4, shown little or no decrease in efficiency (sample 2008-229-3 actually showed an increase in efficiency. Filters that have the pleat structure in versions of the invention are essentially unaffected in their efficiency as measured by the nitrogen purge test. Without wishing to be bound by theory, it is believed
30 that the nitrogen purge test can be used as a measure of deformation of pleats in a filter; similar deformation of pleat may occur during filtration in various cleaning baths and lead to flow decay over time. Versions of filters with the pleat structure in versions of the present invention as described and illustrated by the non-limiting examples resist this deformation as indicated by nearly constant filter efficiency as shown by the results in FIG. 3.

The order of the heights of the secondary pleats between the primary pleats in repeating pleat patterns in versions of the invention is not limited to any particular order as long as the pattern is repetitive. For example moving from left to right, the secondary pleats in FIG. 1 are in the opposite order from those shown in FIG. 5. The order of the secondary pleats between the primary pleats in a cycle of the pleat structure can be arranged in any pattern so long as the pattern is repeated through out the filter; the size of the secondary pleats does not need to be in an increasing or decreasing order.

While the pattern of primary and secondary pleats in versions of the invention is repetitive, it is not required that integral numbers of a pleat cycle, for example (P, P, S1, P, S2...) be present in a filter. For example, where the fit of the pleated filter between the core and cage is facilitated by omitting some pleats, for example but not limited to P and S2 in the final pleat cycle, filters with these pleated filters are considered repetitive for purposes of the claims and specification.

The primary and secondary pleats are made by a pleater. Small variations in pleat size, for example $\pm 5\%$ or less (in some cases $\pm 1\%$ or less) of the average height of a secondary pleat, is considered for purposes of the specification and claims to provide a repeating pattern of secondary pleats.

One version of the invention is illustrated in FIG. 1 and is a pleated filter comprising a pleated microporous membrane that has a repeating pattern of primary pleats and secondary pleats, the primary pleats have a height P which is the distance measured between an inner core of the filter and an outer cage of the filter. The pleated filter includes a first secondary pleat that has a height S1 measured from the cage to the inner peak of the pleat and a second secondary pleat that has a height S2 measured from the cage to the inner peak of the pleat. In the pleated filter, S1 is different from S2 and both S1 and S2 are less than P. The repeating pleat pattern of primary pleats and secondary pleats can be described by the notation (P, P, S1, P, S2...). As illustrated in FIG. 1, S1 has a height that is $P/3$ and S2 has a height that is $2P/3$.

In versions of the invention the microporous membrane can comprise, consist essentially of, or consists of the repeating pattern of primary and secondary pleats.

In some versions of the invention the deterioration or loss of flow through the filter with the repeating pleat pattern following a nitrogen purge treatment is less than 15 percent.

Another version of the invention, for example as shown in FIG. 1, FIG. 4, and FIG. 5, is a pleated filter comprising a pleated microporous membrane that has a repeating pattern of pleats that include primary pleats and secondary pleats. As shown in FIG. 4, the repeating

pattern of pleats has n pairs, n equals 4, of adjacent primary pleats, and $n+1$ primary pleats (P1, P2, P3, P4, P5). Each primary pleat has a height P measured between an inner core of the filter and an outer cage of the filter. The repeating pattern of pleats has $(n-1)$ secondary pleats (S1, S2, S3) between $(n-1)$ pairs of the primary pleats. This is illustrated by three $(n-1)$ secondary pleats between Pair2, Pair 3, and Pair4 in FIG. 4. One pair of primary pleats, Pair1 is absent or without a secondary pleat between P1 and P2. In some versions of the invention the heights of the $(n-1)$ secondary pleats are determined by (P/n) , $(2P/n)$... $((n-1)P/n)$. In some versions of the invention “ n ” is 3, or 4, or 5; in other versions “ n ” is 3.

Although the heights of the secondary pleats in the repeating pattern can be mixed (the same mixed pattern of secondary pleats occurs repetitively), in some versions of the invention the heights of the secondary pleats increases stepwise.

In one version of the invention, n is 3 for the repeating pattern of pleats, the repeating pattern of primary pleats and secondary pleats is designated by $(P, P, S1, P, S2\dots)$, and the height of S1 is $(P/3)$ and the height of S2 is $(2P/3)$.

FIG. 5 illustrates differences in pleat structure between a standard pleat, a $\frac{1}{2}$ M pleat and a pleat structure of a version of the invention; the core side of the pleat structure in these illustrations in on the bottom while the sleeve side is on the top. The core side and sleeve side of the pleated membranes are shown in an illustrated filter cartridge in cross section (inner circle represents a core, outer larger diameter circle represents a cage). The Table contains the same information as FIG. 1.

Although the present invention has been described in considerable detail with reference to certain preferred embodiments thereof, other versions are possible. Therefore the spirit and scope of the appended claims should not be limited to the description and the preferred versions contain within this specification.

CLAIMS

What is claimed is:

Claim 1. A pleated filter comprising:

a pleated microporous membrane that has a repeating pattern of primary pleats and secondary pleats, the primary pleats have a height P measured between an inner core of the filter and an outer cage of the filter, a first secondary pleat that has a height $S1$ and a second secondary pleat that has a height $S2$, where $S1$ is different from $S2$ and both $S1$ and $S2$ are less than P , the repeating pattern of primary pleats and secondary pleats is $(P, P, S1, P, S2\dots)$.

Claim 2. The pleated filter of claim 1 further comprising support layers on one or both sides of said pleated filter material.

Claim 3. The pleated filter of claim 1 where $S1$ is less than $S2$.

Claim 4. The pleated filter of claim 1 where $S1$ is $P/3$ and $S2$ is $2P/3$.

Claim 5. The pleated filter of claim 1 where the microporous membrane consists of the repeating pattern of primary and secondary pleats.

Claim 6. The pleated filter of claim 1 where the deterioration or loss of flow through the filter following a nitrogen purge treatment is less than 15 percent.

Claim 7. A pleated filter comprising:

a pleated microporous membrane that has a repeating pattern of pleats that include primary pleats and secondary pleats, the repeating pattern of pleats has n pairs of adjacent primary pleats, and $n+1$ primary pleats, each primary pleat has a height P measured between an inner core of the filter and an outer cage of the filter, the repeating pattern has $(n-1)$ secondary pleats between $(n-1)$ pairs of the primary pleats and one pair of primary pleats without a secondary pleat therebetween.

Claim 8. The pleated filter of claim 6 where the heights of the $(n-1)$ secondary pleats are determined by $(P/n), (2P/n)\dots((n-1)P/n)$.

Claim 9. The pleated filter of claim 6 where n is between 3, 4, or 5.

Claim 10. The pleated filter of claim 6 where n is 3.

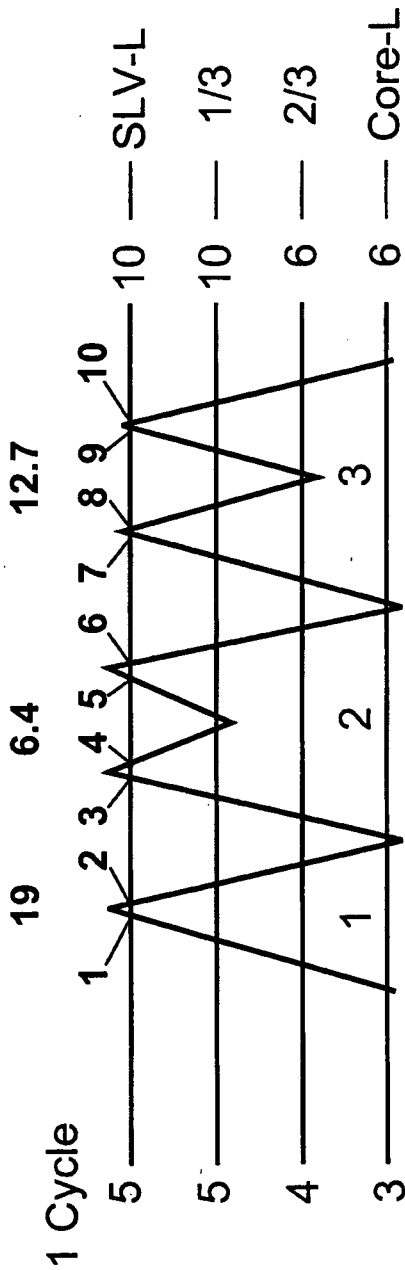
Claim 11. The pleated filter of claim 6 where the heights of the secondary pleats increases stepwise.

Claim 12. The pleated filter of claim 6 where n is 3, the repeating pattern of primary pleats and secondary pleats is P, P, S1, P, S2 and the height of S1 is $(P/3)$ and the height of S2 is $(2P/3)$.

Claim 13. The pleated filter of claim 6 where the deterioration or loss of flow through the filter following a nitrogen purge treatment is less than 15 percent.

Claim 14. The pleated filter of claim 6 where the deterioration or loss of flow through the filter following a nitrogen purge treatment is less than 10 percent.

Structure:



Flow Time (Sec)	Area (cm ²)	Pleats Arrangement	Sample No.	Thickness of the Pleats			
				SLV-L Compression Rate	1/3-L M Valley	2/3-L M Valley	Core-L
436	20,698	1/2 M Pleats	N8M707134(ATE)	0.83	-	0.59	0.62
527	20,760	Dual M Pleats	2008-229-1	0.77	0.64	0.64	0.64
527	20,760	Dual M Pleats	2008-229-2	0.77	0.64	0.64	0.64
527	20,760	Dual M Pleats	2008-229-3	0.77	0.64	0.64	0.64
527	18,081	Dual M Pleats	2008-229-4	0.88	0.74	0.74	0.74

Figure 1

2008-229 20 nm Accelerated N₂ Purge Test

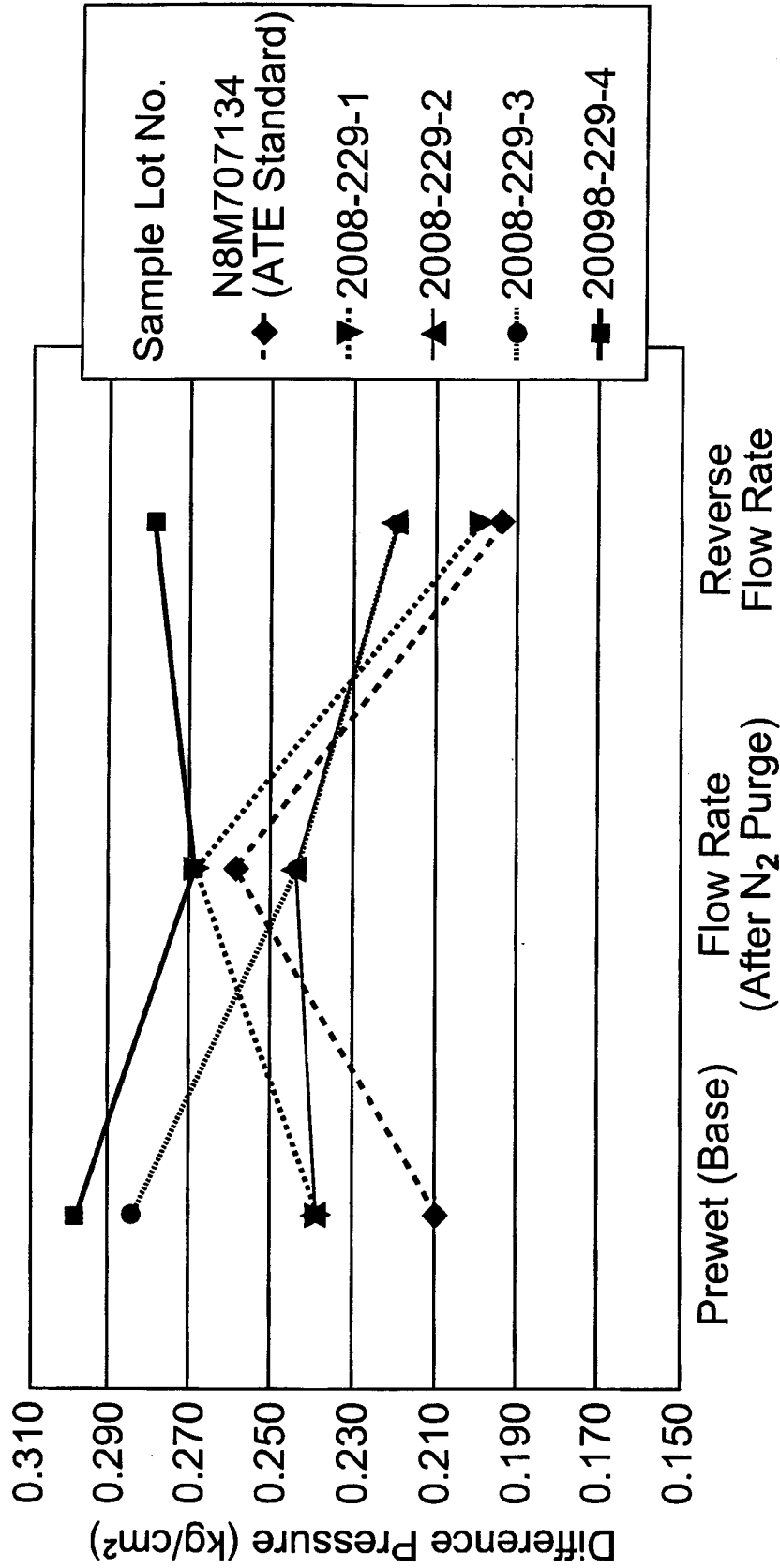


Figure 2

Flux Ratio Evaluation:

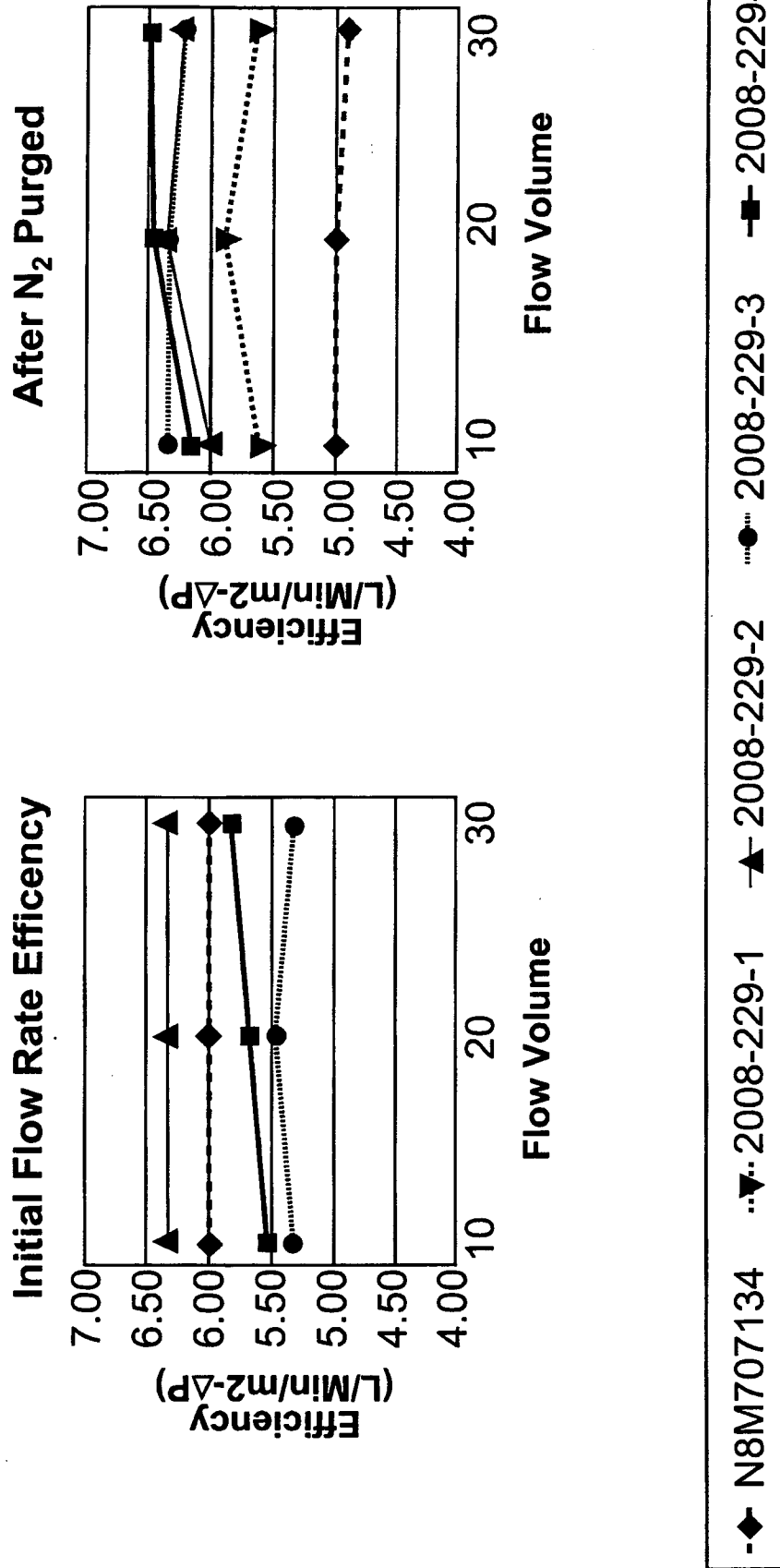


Figure 3

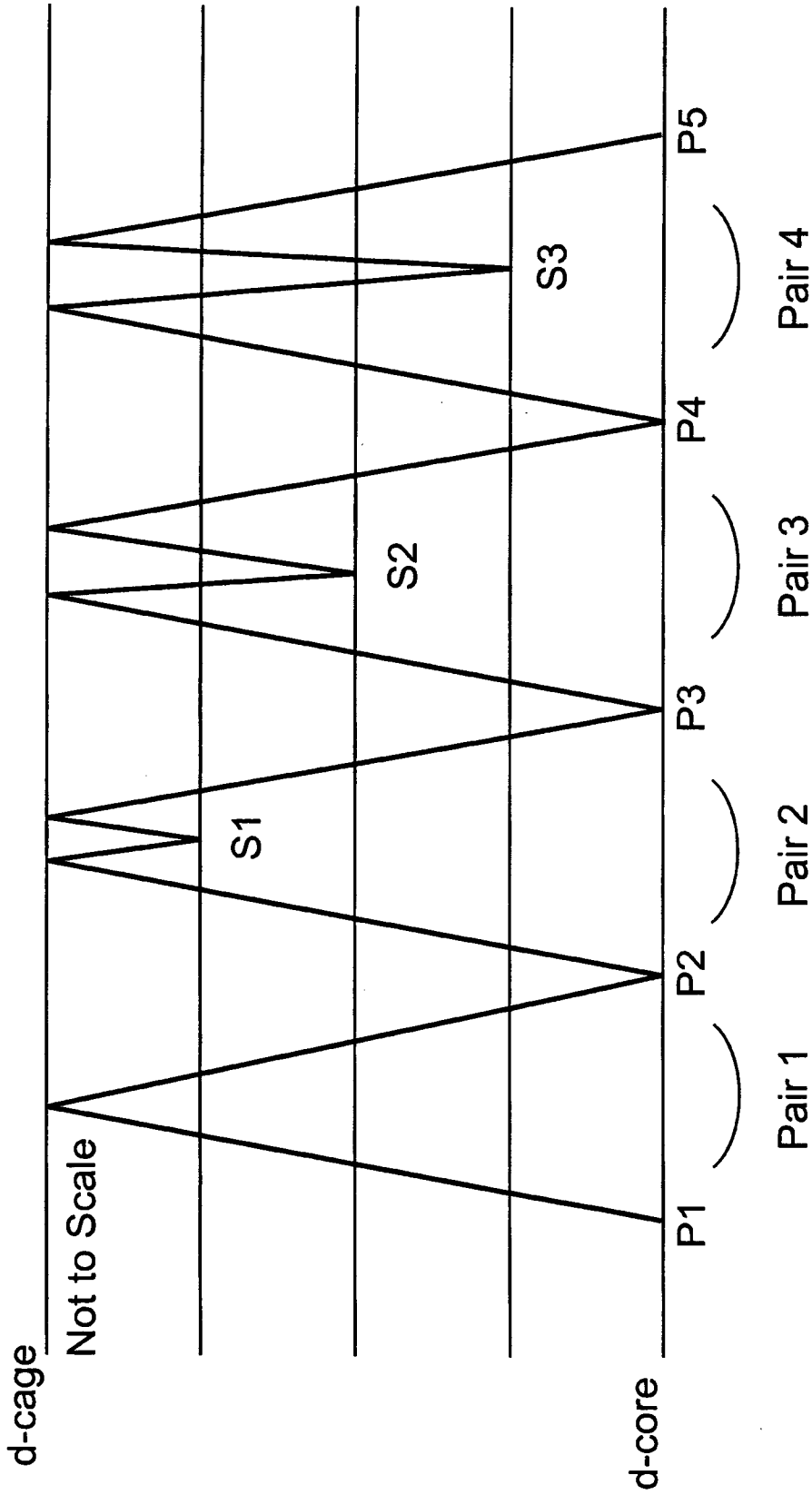


Figure 4

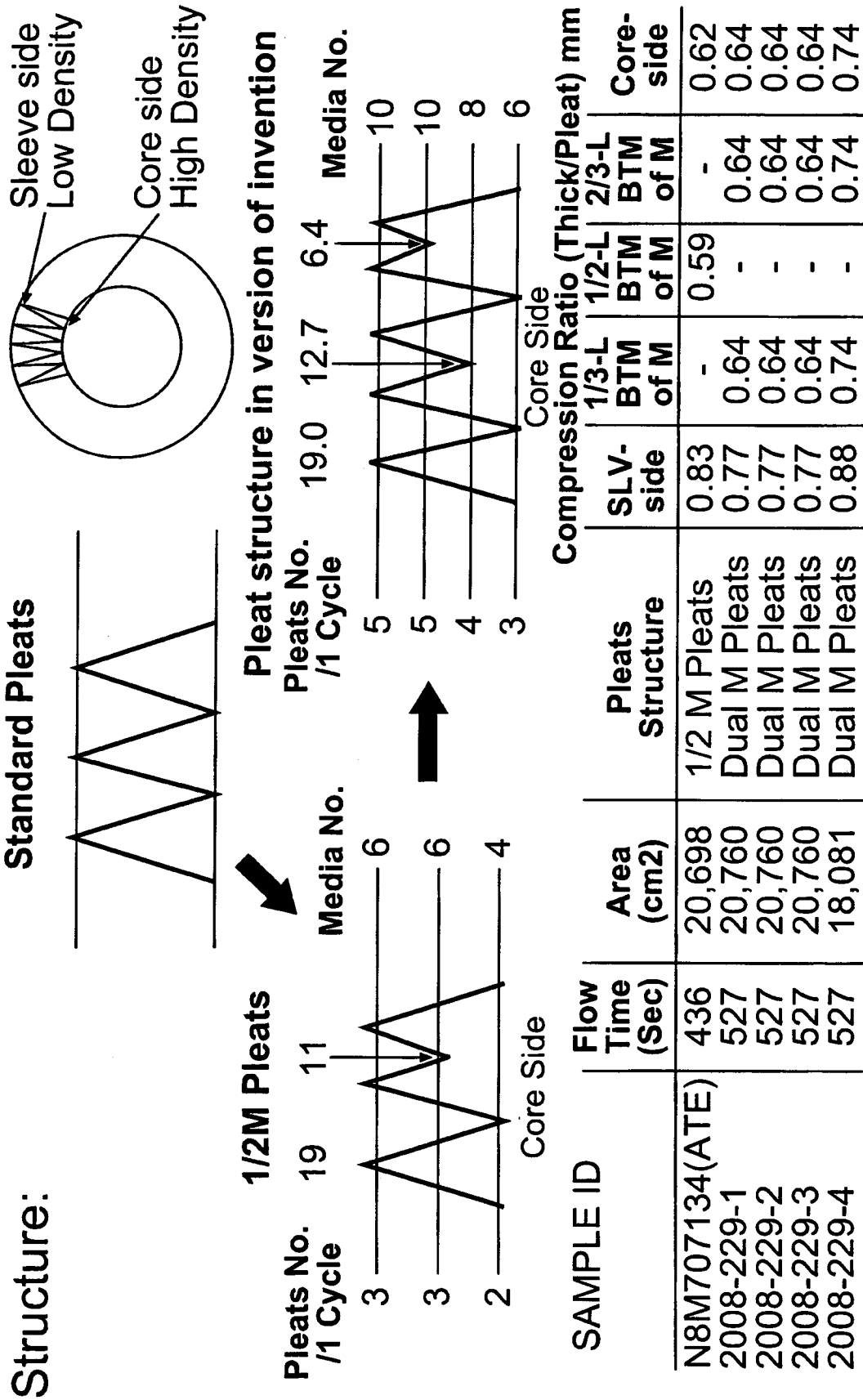


Figure 5

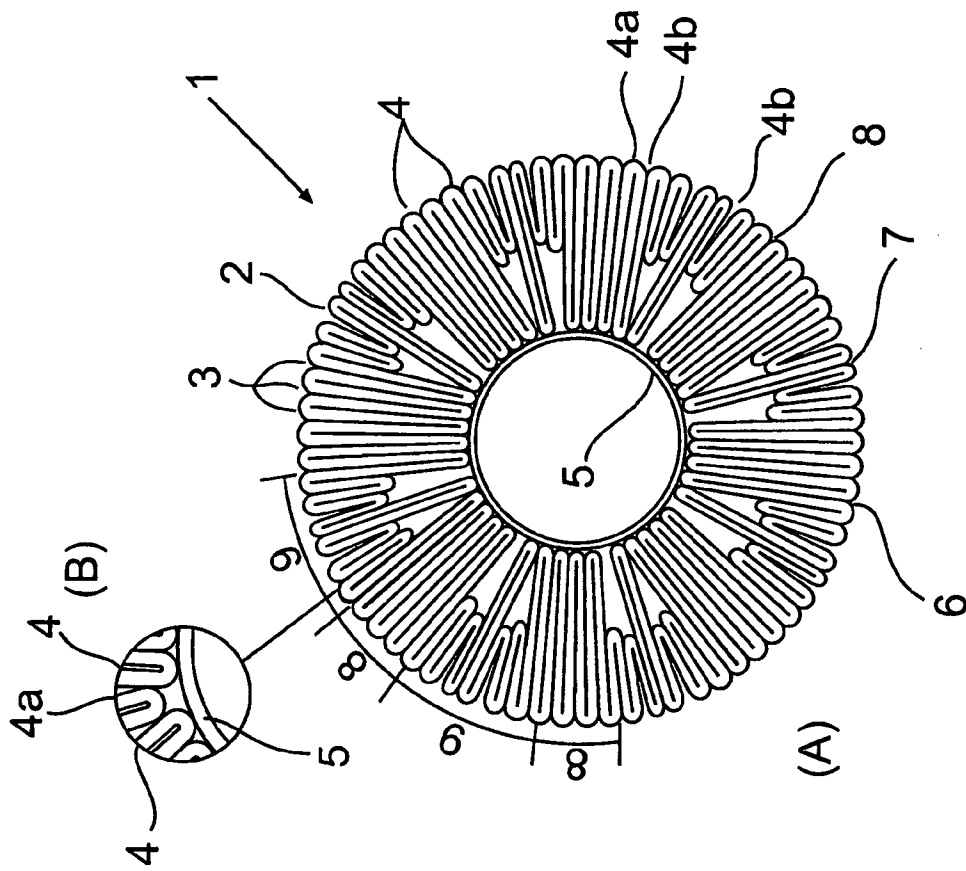


Figure 6
Prior Art