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EP 0578010 A1 **US 6660656 B2**
US 6059935 A **US 5041201 A**
US 4837185 A **US 4539098 A**

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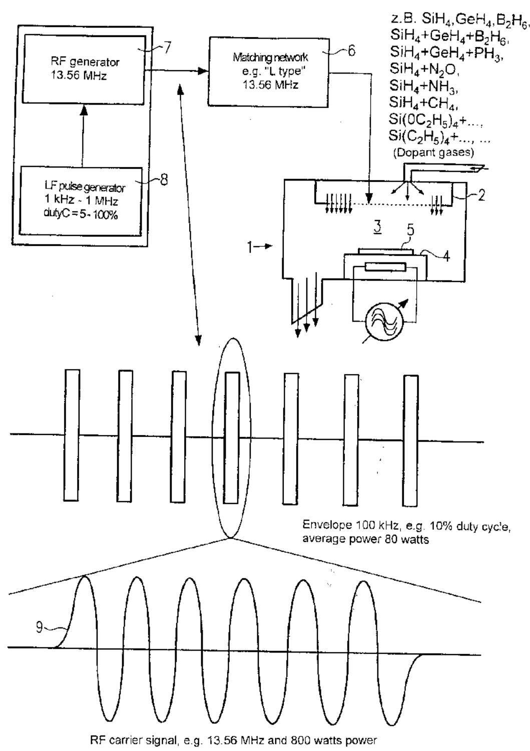
(54) Abstract Title: **Plasma deposition method**

(57) Method for depositing a layer on a wafer via plasma-induced reactions in the vapour phase, where the layer is deposited by radiofrequency excitation of the plasma, by means of radiofrequency power. The radiofrequency power is low-frequency modulated and can be clocked. The excitation may be varied between a radiofrequency character and a low frequency character so that the layer stress minimisation can be performed. An upper showerhead electrode 2 may be used, with a matching network 6 connected between the electrode 2 and the radiofrequency generator 7.



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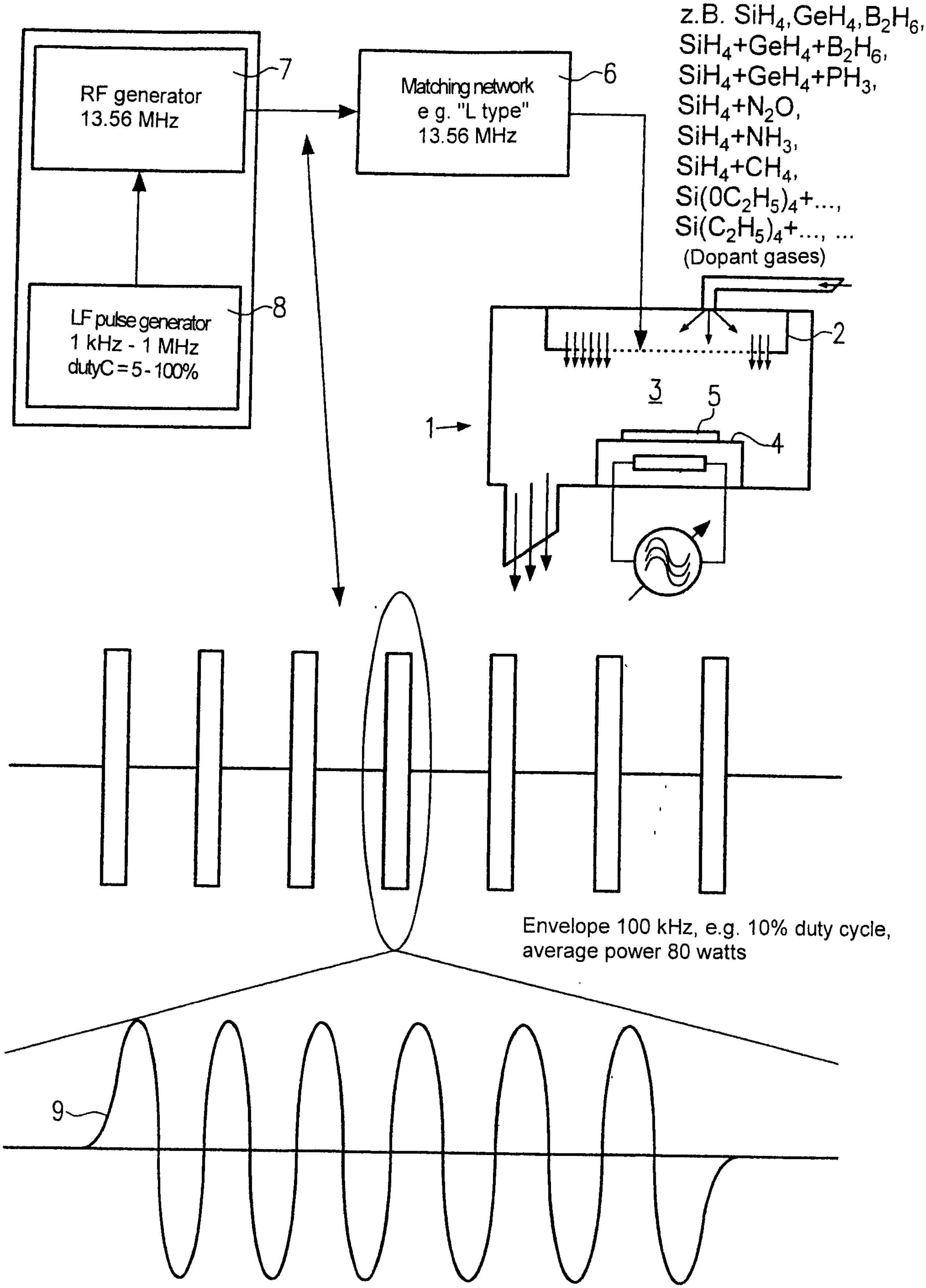

RF carrier signal, e g. 13 56 MHz and 800 watts power

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Plasma Deposition Method

Description

The invention relates to a method for depositing a layer on a wafer by plasma-induced reactions in the vapour phase, particularly one in which the layer is deposited by radiofrequency excitation of the plasma by means of radiofrequency power.

Prior Art

Plasma deposition methods conventionally use reactive plasmas of silanes, germane or other gases, either individually or mixed together (for example SiH_4 and GeH_4 for SiGe deposition) or in conjunction with reaction partners such as N_2O, NH_3, CH_4, C_2H_5, … etc. or in conjunction with dopant gases such as diborane or phosphine … etc., in order to deposit layers (α-Si, α-Ge, α-SiGe, poly-Ge, poly-SiGe, SiC, SiN, SiO, …) on wafers by plasma-induced reactions in the vapour phase. The wafers conventionally lie on an earthed substrate electrode which is heated to a particular temperature, for example $T = 300 \ldots 600°C$. The process gases are conventionally fed into the plasma chamber through an upper showerhead electrode, this being arranged in parallel with the usually earthed substrate electrode and being supplied with radiofrequency and/or low-frequency power. There is also the case of powering the substrate electrode, or the case of powering both electrodes in parallel, that is to say the showerhead electrode and the substrate electrode, in a so-called triode arrangement.

The frequency of the plasma excitation has a crucial effect on the properties of the layers which are deposited, in particular their intrinsic stress properties. For example, it is possible to deposit SiO layers with an compressive intrinsic stress by means of radiofrequency excitation, for example at 13.56 MHz. By means of low-frequency excitation, for example at 380 kHz of for example 100 kHz, it is possible to deposit these SiO layers with a tensile stress. Low-frequency and radiofrequency plasma excitation is often combined in order to deposit stress-free layers, or at least low-stress layers. Stress minimisation is then achieved by selection and optimisation of the strengths of the radiofrequency and low-frequency components of the plasma excitation. This may be achieved, for example, if both the radio frequency and the low frequency can be simultaneously applied and matched to the powered electrode(s) through an elaborate matching network. In this case, the strengths of the low-frequency and radiofrequency plasma-excitation components are simply determined by the power settings of the individual components. Another alternative is to operate the plasma alternately with radio frequency or low frequency in chronological succession. Radiofrequency excitation is selected for a particular period of time, and a low-frequency excitation is selected for the next period of time, etc. The weightings of the two alternating components may be controlled either by their durations or by the power selected for the respective component. Both the radiofrequency generator and the low-frequency generator need their own network for matching to the powered electrode, each of which ensures the impedance matching. With alternating RF or LF operation, however, the two networks do not need to decouple the two generators from each other, since they are not operated simultaneously and they do not therefore have a detrimental effect on each other. To this extent, the matching networks are then less elaborate than the case in which the two generators are to be operated simultaneously.

The requirements of a radiofrequency generator and a low-frequency generator, as well as the associated matching networks for radio frequency and low frequency, in any event entail significant outlay. Added to this, low-frequency plasmas are generally unstable, ignite poorly and may also be poorly matched. These remarks therefore also apply to processes which are determined more strongly by low-frequency excitation than by radiofrequency excitation, that is to say ones in which the properties of the radiofrequency excitation are less important than those of the low-frequency excitation, owing to the weightings which are selected. The problems therefore stem, as is known, from the fact that relatively low ion densities and ion currents are produced with low-frequency excitation, so that high voltages need to be set up across the powered electrodes, which in turn places great demands on the quality of the matching networks being used. If electrical loss paths occur, then the voltages required for ignition and operation of the plasma will no longer be reached, so that instabilities occur, even to the extent that the plasma may be quenched. The matching adjustments critically depend, inter alia, on the frequency of the low-frequency excitation; they are also modified, for example and sometimes very strongly, by the inevitably occurring growths of dielectric layers, that is to say more or less electrically insulating layers, on the powered electrode during the deposition process, so that a further unreliability arises within the process in the form of possible drift phenomena over time.

Low-frequency plasmas are often combined with ignition aids in order to ignite the plasma, for instance a switch-on pulse of high power, and the power value that is actually required is only returned to later. This also leads to great outlay.

Another physically related disadvantage of low-frequency plasmas is the fact that the energy of the ions which are produced is not sharply defined, but rather covers a broad energy spectrum of from 0 up to a peak value, which depends on the selected power. This broad energy distribution of the ions makes it difficult to achieve process optimisation, in particular model-based optimisation. An energy distribution which is defined as sharply as possible for the ions produced in the plasma would therefore be expedient, as is the case with radiofrequency excitation, for example at 13.56 MHz or more preferably at 27.12 MHz or even higher multiples of 13.56 MHz, for example 40.68 MHz.

Advantages of the Invention

The method according to the invention for depositing a layer on a wafer by plasma-induced reactions in the vapour phase, in which the layer is deposited by radiofrequency excitation of the plasma by means of radiofrequency power, is characterised in that the radiofrequency power is low-frequency modulated.

The method according to the invention overcomes the aforementioned disadvantages according to the prior art. Instead of combined low-frequency and radiofrequency excitation of the plasma, it uses a single radiofrequency generator, for example at 13.56 MHz, and a single network for matching, for example at 13.56 MHz, to the powered electrode. By the low-frequency modulation, the character of the excitation can be varied continuously between a radiofrequency situation and a low-frequency situation, so that any required intermediate state of the excitation character can be set up and, for example, layer stress minimisation can thereby be carried out without modifying the carrier frequency and without needing to modify the matching network. Since the plasma power can then be kept constant at a required power value as a time-average, the chemistry of the plasma is not changed by the variation between a radiofrequency situation and a low-frequency situation, because the decomposition of the process gases is primarily contingent on the average power value in the plasma. The variation according to the invention between a radiofrequency situation and a low-frequency situation therefore influences only the physical effects on the wafer surface which are controlled by the ion action, although it does so significantly.

A particular advantage of the method according to the invention, which may be pointed out, is that the ion energy distribution remains sharply defined owing to the high carrier frequency, even when the excitation has a low-frequency character, so long as the radiofrequency power has sufficiently fast leading and trailing edges. Process optimisation with a view to a minimal layer stress, for example, is facilitated by this.

In the method according to the invention, the radiofrequency power is preferably low-frequency modulated with a frequency higher than 1 kHz, in particular higher than 10 kHz, more particularly higher than 10 kHz and less than 1 MHz, even more particularly higher than 10 kHz and less than 500 kHz, even more particularly higher than 50 kHz and less than 200 kHz, even more particularly 100 kHz.

In the method according to the invention, a pulse-to-period ratio, that is to say the duty cycle d, of the modulation of the radiofrequency power can furthermore preferably be selected freely, in particular from a range of between 1% and 100%, more particularly from a range of between 5% and 100%, even more particularly from a range of between 10% and 90%.

For d = 1, a radiofrequency character is then obtained, with which the ion energies are relatively low and the ion currents and densities in the plasma are relatively high. For small values of d, for example d = 0.2 or d = 0.1 or d = 0.05, a low-frequency character is obtained, for which the ion energies are relatively high and the average ion currents and densities are relatively low. A required intermediate state for carrying out layer stress minimisation may, for example, be set up with medium d values. The duty cycle parameter d significantly influences the aforementioned physical effects on the wafer surface which are correlated with the ion action, without modifying the chemistry of the plasma, since the plasma power is kept constant at a required power value as a time-average. Even if a low-frequency character is set up by the duty cycle parameter d, this changes nothing in respect of the sharp definition of the excitation of the ion energy distribution.

In accordance with the method according to the invention, the radiofrequency power preferably has a frequency of from 1 to 50 MHz, in particular 13.56 MHz or 27.12 MHz. The radiofrequency power preferably has a peak pulse power of up to 1000 watts according to the invention, more preferably up to 2000 watts.

The radiofrequency power is preferably low-frequency modulated according to the invention by means of a pulse signal, which more preferably has approximately square-wave leading and trailing edges that have a rise time of less than 1 μs, more preferably between 0.1 μs and 0.3 μs. According to the invention, the low-frequency modulation preferably causes periodic switching off and switching on of the radiofrequency power.

According to the invention, the wafer preferably lies on an earthed substrate electrode of a device for depositing a layer on a wafer, and process gases are fed through an upper showerhead electrode, arranged in parallel with the substrate electrode, into a plasma chamber of the device for depositing a layer on a wafer. According to the invention, the radiofrequency power is preferably produced by a radiofrequency generator and put in through a matching network to a powered electrode, preferably the upper showerhead electrode, of a device for depositing a layer on a wafer.

The excitation mechanism according to the invention will be described below. Let P be the average plasma power put in, which is intended to be kept constant for a particular process, let d be the freely selected pulse-to-period ratio, that is to say the duty cycle parameter, let p be the peak pulse power resulting from P and d, let u be the voltage at the showerhead electrode, corresponding to the energy of the ions generated in the plasma, let i be the pulsed ion current and let I be the time-average of the ion current. The pulse frequency must be high enough to permit time averaging of the ion current, that is to say the physical effects of the current pulses on a surface, for example on the wafer surface, must correspond to the effect of an average current flow which is constant over time. For a carrier frequency of 13.56 MHz, this happens with frequencies above 1 kHz, and reliably with frequencies above 10 kHz. Pulse repetition rates of 100 kHz are preferably used in the method according to the invention.

With the assumption that the plasma impedance X changes only little with the plasma power, that is to say Ohm's law approximately applies, the following are satisfied:

$$p = \frac{P}{d} \qquad u = \sqrt{X\frac{P}{d}} \propto \sqrt{\frac{1}{d}} \qquad i = \sqrt{\frac{1}{X}\frac{P}{d}} \qquad I = \sqrt{\frac{1}{X}Pd} \propto \sqrt{d}$$

If, with a constant average power P, the pulse-to-period ratio d is reduced and the peak pulse power p is scaled up accordingly, then this increases the energy u of the ions generated in the plasma $\propto \sqrt{\frac{1}{d}}$ and decreases the average current $I \propto \sqrt{d}$. With an equal power input, it is therefore possible to use the duty cycle parameter d to select whether a high ion energy with a correspondingly low average ion current, or a low ion energy with a correspondingly high average ion current, is required. The time averaging, as is permissible for the ion current at pulse frequencies of > 10 kHz and which correctly reflects the physical reality on the surface in question for such pulse frequencies, is unimportant for the ion energy since the physical effects of the ion action correlate not with the time-average value, but rather with the energy of each incident ion. A pause without any ion action, or the action of ions with a very low energy, is neutral in respect of the result, but what is crucial is the ion energy in the process phases in which action of ions with high energy actually takes place, that is to say during the pulse phases. The duty cycle parameter d therefore provides a degree of freedom, the effect of which corresponds to adjustability of a quantity analogous to a "plasma impedance", which is obtained from the relation of the ion energy with the average ion current. The duty cycle parameter d does not therefore arbitrarily vary the plasma impedance, but rather a "peak voltage or ion energy/average current" relation similar to an "impedance". The actual plasma impedance X is essentially determined by the carrier frequency, for example 13.56 MHz, and remains approximately fixed when there are variations of the duty cycle parameter d, as assumed above, since the carrier frequency as the quantity predominantly determining the impedance remains fixed.

The character of the plasma excitation can therefore be selected freely between "radiofrequency" and "low-frequency" through the duty cycle parameter d, without needing to modify other characteristic quantities, for example the matching by means of a matching network. In particular, no problems of ignition or stability arise in the plasma even with a low-frequency character of the plasma excitation, insulation layers deposited on the powered electrode have little or no perturbing effect by virtue of the high carrier frequency, and the generated ion energy is sharply defined even for the low-frequency case. According to the invention, the case of low-frequency excitation is emulated by small values of the duty cycle parameter d and the advantages of the low-frequency excitation are obtained without having to tolerate its disadvantages.

Another advantage of pulsed operation, in particular with a low duty cycle parameter d and a high peak power p in the pulse peaks, is that of improved plasma stability, particularly with high process pressures, and above all in respect of any undesirable occurrence of current channels or discharges between the electrodes, so-called "arcing". For many processes, for example deposition of poly-SiGe (polycrystalline silicon-germanium) by means of a process gas mixture of silane SiH_4 and germane GeH_4, optionally in conjunction with dopant gases such as B_2H_6 or PH_3, for example with a wafer temperature of from 500°C to 600°C, in particular 550°C, a high pressure of for example from 10 to 500 mbar, in particular about 100 mbar, is advantageous as a "near-atmosphere" plasma for a high deposition rate. On the basis of the "Paschen curve", however, such high-pressure plasmas are inclined to form discharges with the requisite narrow electrode spacings, which makes the plasma support of SiGe deposition substantially more difficult or even impossible. Although deposition at 550°C under atmospheric conditions is also possible purely in a thermally induced way, and does not necessarily require plasma support, plasma support does have great advantages for control and improvement of the deposition rate and the layer quality of the deposited poly-SiGe layers. The pulsing of the plasma, in particular with a low duty cycle d and high peak pulse powers p, effectively prevents "arcing" so that the permissible working pressure of a plasma is increased significantly, which in turn offers advantages in respect of the achievable deposition rates. This upwards extension of the working pressure range to near atmospheric conditions is achieved without additional measures other than the aforementioned pulsing, and therefore entails no additional outlay. A further advantage, in the form of higher possible process pressures, can therefore be achieved by the technique according to the invention with no outlay.

Drawing

Other advantages of the invention will be found in the following description of the drawing. The drawing represents an embodiment of the invention by way of example. The drawing, the description and the claims contain many features in combination, or referred to as a preferred exemplary embodiment of the invention. The person skilled in the art will also expediently consider the features individually and/or combine them to form further useful combinations.

Figure 1 shows a schematic diagram of the plasma deposition method according to the invention.

Description of the Exemplary Embodiment

The upper part of Figure 1 shows a plasma deposition system which is known in principle, and in which for example SiH_4, GeH_4, SiH_4 + GeH_4, SiH_4 + GeH_4 + B_2H_6, SiH_4 + GeH_4 + PH_3, …, SiH_4 + N_2O, SiH_4 + NH_3, SiH_4 + CH_4, $Si(OC_2H_5)_4$ + …, $Si(C_2H_5)_4$ + …, etc., are supplied as process gases to an upper showerhead electrode 2 and fed through it into a plasma chamber 3. The upper showerhead electrode 3 is arranged in parallel with an earthed substrate electrode 4, on which there is a wafer 5.

The radiofrequency power produced according to the invention is applied to the upper showerhead electrode 2 through a conventional matching network 6, for example of the "L type", for example for 13.56 MHz from an RF generator 7 which produces a radiofrequency carrier signal of for example 13.56 MHz. The RF generator 7 allows modulation of its radiofrequency carrier signal, having for example a carrier frequency 13.56 MHz, with approximately square-wave leading and trailing edges. A low-frequency LF pulse generator 8 is used for modulating the radiofrequency carrier signal, here with a freely selectable frequency of for example from 1 kHz to 1 MHz, in particular 100 kHz, and an adjustable duty cycle of for example from 5% to 100%. The radiofrequency generator 7 and the low-frequency pulse generator 8 may also be integrated in a single device. The modulation of the radiofrequency carrier may be regarded as periodic switching on and off, or clocking, of the radiofrequency generator 7 by the low-frequency pulse generator 8.

The rise time of the leading and trailing edges should be significantly less than 1 μs. Values of from 0.1 to 0.3 μs can be achieved with commercially available generators for a carrier frequency of 13.56 MHz. According to the invention, the pulse repetition rate should be between 1 kHz and 500 kHz, in particular between 50 kHz and 200 kHz, preferably at 100 kHz. With the low-frequency pulse generator 8 according to the invention, the pulse-to-period ratio can be adjusted over as wide a range as possible, for example between 1% and 100% or, as shown in Figure 1, between 5% and 100%, or at least between 10% and 90%. The maximum peak pulse power of the radiofrequency generator 7 should extend up to 1000 watts, preferably up to 2000 watts, and likewise be freely selectable up to this value.

The middle and lower parts of Figure 1 show a pulse train as is produced according to the invention and can be applied to the powered showerhead electrode 2 of the plasma deposition system 1. Pulses of the radiofrequency carrier signal, for example at 13.56 MHz, are generated with a repetition rate of for example 100 kHz and a duty cycle d = from 0.05 to 1 and a constant average power, which corresponds to the plasma power required in the process. The average power is 80 watts in the example which is given. If the duty cycle parameter d is selected to be 10%, then the required peak pulse power is 800 watts. The RF generator 7 accordingly generates a radiofrequency carrier signal 9 with a frequency of for example 13.56 MHz and a voltage amplitude which corresponds to a power of for example 800 watts, as represented at the bottom in Figure 1. The clocking of the carrier signal of the radiofrequency generator 7 by the low-frequency pulse generator 8 is carried out at 100 kHz and with a pulse-to-period ratio of 10%, so that the carrier signal is periodically switched on and off, or clocked, for the low-frequency modulation, as shown in the middle of Figure 1.

Patent claims:

1. Method for depositing a layer on a wafer by plasma-induced reactions in the vapour phase, in which the layer is deposited by radiofrequency excitation of the plasma by means of radiofrequency power, characterised in that the radiofrequency power is low-frequency modulated.

2. Method according to Claim 1, characterised in that the radiofrequency power is low-frequency modulated with a frequency higher than 1 kHz, in particular higher than 10 kHz, more particularly higher than 10 kHz and less than 1 MHz, even more particularly higher than 10 kHz and less than 500 kHz, even more particularly higher than 50 kHz and less than 200 kHz, even more particularly 100 kHz.

3. Method according to Claim 1 or 2, characterised in that a pulse-to-period ratio (d) of the modulation of the radiofrequency power can be selected freely, in particular from a range of between 1% and 100%, more particularly from a range of between 5% and 100%, even more particularly from a range of between 10% and 90%.

4. Method according to one of the preceding claims, characterised in that the radiofrequency power has a frequency of from 1 to 50 MHz, in particular 13.56 MHz or 27.12 MHz or 40.68 MHz.

5. Method according to one of the preceding claims, characterised in that the radiofrequency power has a peak

pulse power of up to 1000 watts, preferably up to 2000 watts.

6. Method according to one of the preceding claims, characterised in that the radiofrequency power is low-frequency modulated by means of a pulse signal.

7. Method according to Claim 6, characterised in that the pulse signal has approximately square-wave leading and trailing edges, which have a rise time of less than 1 μs, preferably between 0.1 μs and 0.3 μs.

8. Method according to one of the preceding claims, characterised in that the low-frequency modulation causes periodic switching off and switching on of the radiofrequency power.

9. Method according to one of the preceding claims, characterised in that the wafer lies on an earthed substrate electrode of a device for depositing a layer on a wafer, and process gases are fed through an upper showerhead electrode, arranged in parallel with the substrate electrode, into a plasma chamber of the device for depositing a layer on a wafer.

10. Method according to one of the preceding claims, characterised in that the wafer lies on an RF-supplied substrate electrode, opposite which an earthed showerhead electrode is placed as the gas inlet.

11. Method according to one of the preceding claims, characterised in that the wafer lies on an RF-supplied substrate electrode, opposite which a likewise RF-supplied showerhead electrode is placed as the gas inlet.

12. Method according to one of the preceding claims, characterised in that the radiofrequency power is produced by a radiofrequency generator and put in through a matching network to a powered electrode, preferably the upper showerhead electrode, of a device for depositing a layer on a wafer.

13. Method according to one of the preceding claims, characterised in that the wafer temperature is from 500°C to 600°C, in particular 520°C - 560°C, a gas mixture comprising at least SiH_4 and GeH_4 is supplied, and the process pressure is from 10 to 5 mbar, in particular from 10 to 100 mbar.

14. A method for depositing a layer on a wafer substantially as herein described with reference to the accompanying drawings.

The Patent Office

INVESTOR IN PEOPLE

Application No: GB0408257.4 **Examiner:** Marian Challis

Claims searched: 1-14 **Date of search:** 28 July 2004

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular reference
X	1-4,9-12	US 4539098 A (TAKAGI)Figures 1-10, columns 3-5
X	1-4,6,8,9,12	US 6660656 B2 (CHEUNG) Figures 1-11, columns 3 and 15
X	1-6,8	US 4837185 A (YAU) Figures 1-5, columns 3-5
X	1-4,6,8-12	EP 0578010 A1 (TEXAS) Figure 1, pages 5-7
X	1-6,8,9	US 6059935 A (SPENCE) Figures 1-11, columns 9,10 and 12
X	1-4,8,12	US 5041201 A (YAMAZAKI) Figure 1, columns 2 and 3

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC[W] :

C7B

Worldwide search of patent documents classified in the following areas of the IPC[07]

C23C

The following online and other databases have been used in the preparation of this search report

PAJ, WPI and EPODOC