TECHNICAL THIN FILM FORMATION METHODS IN LOW TEMPERATURE PLASMA

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ABSTRACT

The relation between the nucleation and growth of thin films, and the deposition variables is presented. This relation serves as a rough guide in the preparation of films with particular properties. The selection of the deposition technique for making the film is one of the fatal factors that should precisely be considered. The properties and applications of low pressure low temperature plasma are given. The formation of Si-N (Silicon-Nitrogen) thin film on silicon substrate at low pressure low temperature by plasma CVD by only using silane gas diluted in nitrogen without a need for any carrier gases is presented. The films could be obtained with good reproducibility and a relatively high transparency to visible light but with low mechanical strength due to large tensile residual film stress. Such a thin film might be suitable for many microelectronics applications, such as x-ray lithography.

Keywords: Thin Film, CVD , Low Temperature , low pressure, Silicon-Nitrogen .

INTRODUCTION

The formation of thin films on a substrate by deposition is basically a phase change phenomenon involving nucleation and growth with the constraints of the substrate [1-3]. In principle, by controlling the nucleation and growth on the substrate, any of the thin films can be obtained and the film structure and composition can be confirmed by the characterization techniques. In practice, because there are too many variables in thin film deposition that can affect the nucleation and growth, we must know how to control them during the deposition. Putting aside the complications of the film deposition, there should be a rather simple relationship between deposition variables and thin film nucleation and growth to serve as a rough guide in the preparation of films with particular properties. Besides, the most suitable deposition technique for making the film should precisely be selected, for example, whether it is by electron beam heating or by rf sputtering or by rf plasma and so on [4]. Furthermore, if the film is susceptible to an external field, we should consider whether the presence of such an external field is helpful or not [5-6].

In the second part of this paper the properties and applications of low pressure low temperature plasma are given. At first some aspects of plasma generation are discussed including the electrode structures used in commercial plasma equipment. The two major areas of application for low pressure low temperature plasma are described, i.e. plasma deposition and plasma etching of materials.

In the third part one of the recent applications of low temperature low pressure plasma, namely, the formation of a Si-N thin film on silicon substrate is presented. Such a thin film might be suitable for many microelectronics applications, such as x-ray lithography.

FILM DEPOSITION

Deposition Variables

Table 1 illustrates a simple relationship between the deposition variables and parameters of nucleation and growth. It indicates that the deposition variable in the left-hand column has a one-to-one correspondence to the parameters of nucleation and growth in the right-hand column [1,2]. A lowering of vacuum pressure corresponds to an increase of the degree of purity. Supersaturating goes up with deposition rate, but undercooking increases with decreasing substrate temperature. The selection of a substrate that allows epitaxial film growth means that the film-substrate interfacial energy has the lowest value at the epitaxial condition and any deviation from this condition tends to increase the interfacial energy and the barrier of nucleation.

Table 1 Deposition variables

Deposition variables	Parameters of nucleation and growth
Vacuum pressure	impurity content
Deposition rate	supersaturation
Substrate temperature	undercooling
Substrate structure	interfacial energy

Whether the epitaxial film forms a three-dimensional nucleus or a two-dimensional uniform layer on the substrate depends on the wetting condition, which is governed by the interfacial energies involved. On the other hand, a film on a glass substrate will show much less dependence of interface energy on the film orientation.

It is well-known that an increase in impurity content, supersaturation, and undercooling and a decrease in interfacial energy will increase the rate of heterogeneous nucleation [7]. Thus, the combination of a poor vacuum, an increase in deposition rate, and a decrease in substance temperature will lead to the formation of fine grained thin films (or amorphous films) on a glass substrate. On the contrary, the deposition of an epitaxial film requires high vacuum, slow deposition rate, high substrate temperature, and single-crystal substrate with a low Miller index's surface that has small mismatch with the film. What in reality leads to the formation of an epitaxial film is not to reduce the rate of nucleation to that of one nucleus but rather to increase the oriented nucleus so that all the nuclei on the substrate have the same orientation. It should be pointed out that in the deposition of an alloy film, the partial vapor pressure becomes an important variable. To further illustration of the simple relationship discussed above, a list of the conventional deposition conditions for obtaining various kinds of thin films is given in Table 2.

Deposition Techniques

The deposition techniques can be put in three general categories:

a-Physical methods (sputtering techniques)
b-Chemical methods (CVD)
c- Hybrid methods (physical-chemical)

Table 3 gives a brief comparison on the common deposition techniques [1]. In relatively recent years glow discharge has been utilized in a practical way to make a special coating on metals. This technique has some advantages such as flawless thin coating, good adhesion to the substrate, chemical inertness, and low dielectric constant.

LOW TEMPERATURE LOW PRESSURE PLASMA

There are many structures prepared in materials today for application in the electronics and optics industries that just cannot be produced without the use of low energy plasma methods for the deposition and etching of those materials [8]. Thus, silicon nitride layers for use passivation layers in silicon integrated circuits or as capacitive material on hybrid circuits for microwave circuitry can only be prepared with the necessary properties if deposited by either plasma assisted chemical vapor deposition methods or by reactive sputtering techniques.

Low Energy Plasma

Alongside the development of equipment and processes for low energy plasma techniques there have naturally been efforts to understand and explain the mechanisms occurring in the gases at pressures of 0.1-100 Pa energized by ac power up to a few kilovolts that produce the state known as low energy plasma. Most of the recent plasma processing is achieved by the utilization of glow discharge phenomena in suitable metal, glass or quartz reaction chambers to carry out :(i) physical transfer of material by surface ion bombardment

Table 2 Conventional thin film deposition conditions

Deposition variables	Epitaxial film single crystal (Ag-NaCl)a	Textured film ($Pb-SiO_2$)a	Randomly oriented film fine grain ($CrSi_2$)a	Amorphous film (a-Si- Si)a
Vacuum pressure (Torr)	10^{-9}	10^{-7} to 10^{-9}	10^{-5}	10^{-5} to 10^{-9}
Deposition rate (A sec^{-1})	1 to 10 (slow)	10 to 100 (medium)	100 (fast)	> 100 (fast)
Substrate temperature (°C)	350 (limited by the decomposition of NaCl)	above the half-melting point of the metal	room temperature or liquid nitrogen temperature	room temperature or liquid nitrogen temperature
Substrate structure	single-crystal with good lattice match with the film	amorphous	amorphous or polycrystalline metal sheet	amorphous or crystalline

Table 3 Deposition techniques

Deposition technique	Advantages	Disadvantages
Resistance heating evaporation	Easy setup for low melting materials	Alloy with filament
Electron gun evaporation	Apply to most metallic and semiconductor elements. Produces amorphous elemental semiconductors	Refractory metals and carbon ;oxide difficult to evaporate
Sputtering	Deposit conducting as well as insulating materials; film composition is related to target composition. Produce amorphous metallic and semiconductor Easy to apply a biased field	Ar or any other sputtering gas atoms and molecules incorporated in the film Usually high substrate temperatures , intermixing of film and substrate cause damage to substrate surface
Chemical vapor deposition	Device quality epitaxial layer with electrical activity; can also deposit polycrystalline layers	More elaborate set up Gas flow rate adjustment critical; high substrate temperature
Molecular beam epitaxy	High-quality compound films	Elaborate set up
Electro-deposition	Wide range of film and large area of uniform thickness	Useful mostly to metallic films and impurity problems
Liquid phase epitaxy	Good-quality compound films	Concentration control and reproducibility problems
Ion-beam techniques	Precision control of deposition parameters	Slow deposition rate and elaborate set up

(sputtering) or (ii) chemical transfer of material from combination of surface ion bombardment and gas phase or gas-surface chemical reactions of ions or radicals.

It is obvious that the energies of electrons in such a plasma depend on the frequency and power of the applied electrical power but estimates are that mean electron energies of 12 eV are typical with a small fraction of electrons having energies of > 100 eV for a frequency of 13.5 MHz at a power density below 1 W cm^{-2}. Because of the low electron mass, the electrons are capable of high energies without raising the physical temperatures of the gas and gaseous ions present to more than ~ 500 °K- a distinct advantage when it is necessary to process thermally sensitive materials such as gallium arsenide. Electrons with energies of 12 eV can be created by the application of electric fields of 10 V cm^{-1} which are easily achieved under argon gas conditions of 0.1 Pa pressure, energized through simple parallel plate metal electrodes to give electrical power density of 1 W cm^{-2} at 1 kV. Thus, since the first ionization potential of argon is 15.7 eV it is possible to create conditions for the gas phase reaction as shown below, especially when it is considered that the probability of an electron colliding with an argon atom is 0.4 per mm of path length at a gas pressure of 10 Pa [9].

$$e + Ar \xrightarrow{15.7\ eV} Ar^{+} + 2e \quad ,$$

$$e + Ar^{*} \xrightarrow{4.2\ eV} Ar^{+} + 2e$$

Similarly in gases for useful chemical reaction the following are known to occur:

$$e + Cl_2 \xrightarrow{1\ eV} Cl^{-} , \qquad Cl_2 \xrightarrow{2.3\ eV} Cl + Cl$$

$$e + CF_4 \rightarrow 2e + CF_3^{+} + F$$

$$C - Cl \xrightarrow{3\ eV} C + Cl$$

which produce ions and radicals at relatively low energies.

Electrode Configurations

The manner in which the species in an activated gas mixture are directed towards surfaces and substrates in a reactor is determined by the frequency of electrical power, by the voltage distribution created in the reactor, by the electrode configuration employed.

Three basic electrode systems are used:

(i) electrodes external to the reactor (usually tubular or barrel shaped).

(ii) substrate placed on an internal earthed electrode with the electrical power applied to the system through an internal planar electrode parallel to the earthed electrode-a parallel plate system.

(iii) substrate placed on an internal activated electrode-a reactive ion system.

Systems (i) and (ii) have been used for both deposition and etching processes whereas system (iii) has generally been used for etching only.

It is usually considered that plasma potentials and movement of ions play a minor part in reactions in tubular reactors of type (i) where deposition or etching is brought about by reactions of neutral atoms and radicals. Such systems have been used: (a) to deposit silicon from silicon oxides and nitrides from silane, silane/oxygen or silane/ammonia mixtures, and (b) to etch certain metals, silicon, silicon oxide and nitride by fluoro-carbon gas mixtures.

In parallel plate and reactive ion systems however, voltages up to several hundred volts can exist between the plasma and particular surfaces including the substrate in the reactor. Experiments by Coburn et al. [10] have shown that such voltages create conditions at surfaces that enhance chemical reaction by activation of the surface and removal of intermediate products from the surface by ion bombardment.

The particular voltages created between plasma and substrate depend on the gas mixture used, electrode arrangement, frequency of power and the gas pressure employed. Consequently, as the surface reactions depend quite critically on the voltages and the nature and energy of species in the plasma it is useful to determine and control such parameters.

Applications

When a chemically inert gas is used to create a plasma containing Ar^+ ions, which are induced by voltage distributions to bombard the target material, then physical sputtering of that material occurs. This is applied quite extensively in the IC industry to produce inter-connection layers at deposition rates of 1 μm min^{-1} for aluminum/silicon/copper mixtures on silicon circuits. All materials can be physically sputtered but usually at slow rates.

Some materials are produced from gases alone in a gaseous plasma without the application of a sputtering mechanism . This process is known as CVD , i.e. chemical vapor deposition. Such reactions may also occur without plasma activation, but on the expense of applying higher temperatures. It should be mentioned that plasma activated gas mixture deposition has drastic effects on the structure of the deposited layers [11].

The attractions of etching materials with plasma activated gas mixtures stem from: (i) selective etching can be carried out, e.g. Si etched but not SiO_2, and vise versa; (ii) etch profiles with vertical sides can be produced (anisotropic etching); (iii) handling is much easier than liquid solutions. Ephrath and Petrillo [12] have made a particular study of the reactive ion etching (RIE) of silicon dioxide with (CF_4 + H_2) mixtures. Similarly, the etch conditions affect the anisotropy.

THE FORMATION OF SI-N THIN FILM BY LOW TEMPERATURE LOW PRESSURE CVD PLASMA

Silicon compounds such as SiC (silicon carbide) [13] and Si-N (silicon-nitrogen) [11,14] are suitable materials for x-ray mask in an x-ray exposure system with Si target, because of their high transparency to S--K x-ray (7.13 A). However, each material mentioned above has a serious demerit such as low optical transparency, poor productibility and low mechanical strength. All of that work was performed at temperatures higher than 300° C. In this field, we could deposit Si-N thin films at room temperature without heating the substrate. Proper cleaning of the substrates prior to deposition both chemically and in argon plasma is necessary to ensure good adhesion and improve of the electrical properties of the films. The experimental apparatus used in this study is schematically shown in Figure 1. The glow discharge was created through an external capacitive coupling system and operated by an rf frequency of 13.56 MHz. The rf excited plasma was adjusted at some distance from the substrate, thus minimizing the direct field of excitation around the substrate.

Only silane gas at a concentration ranging from 10 to 40% in N_2 was used, with a total flow rate of 400-200 ml min^{-1} . The pressure was as low as less than 20 Pa and the discharge power level at 30-50 W. Table 4 represents the deposition conditions of some films. The deposition rate showed a moderate value of about 30 nm min^{-1}. Infrared spectra showed basically the dominant Si-N absorption based centering near 870 cm^{-1}. Generally speaking, silicon-nitrogen films prepared by this LPCVD with such a good reproducibility have a relatively higher transparency to visible light but low mechanical strength due to large tensile residual film stress.

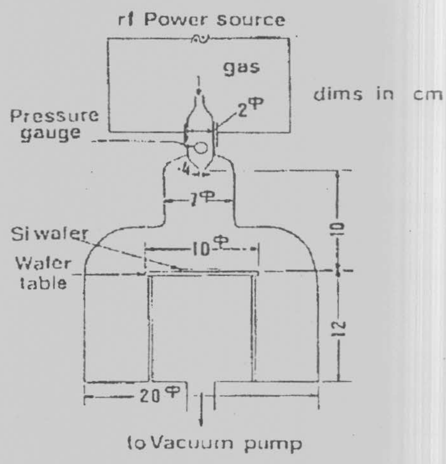

Figure1 Schematic diagram of the experimental apparatus

Table 4 The deposition conditions of some films

Discharge power (W)	Total pressure (Pa)	SiH_4/N_2	Comments
30	15	12%	not stable
40	14	20%	relatively stable
40	16	30%	relatively stable
40	24	33%	stable & transparent
50	20	30%	stable & transparent
50	16	30%	stable & transparent

CONCLUSIONS

There is a correspondence between the deposition variables and the parameters of nucleation and growth. The control of the deposition variables during the deposition is the most important factor affecting the nucleation and growth.

The glow discharge has some advantages such as flawless thin coating, good adhesion to the substrate, chemical inertness, and low dielectric constant. There are many structures prepared in materials today for application in the electronics and optics industries that just cannot be produced without the use of low energy plasma method, for both the deposition and etching of those materials. The manner in which the species in an activated gas mixture are directed towards surfaces and substrates in a reactor is determined by the frequency of electrical power by the voltage distribution created in the reactor by the electrode configuration employed.

Silicon nitrogen films prepared by a commercial rf plasma CVD at low temperature with good reproducibility could be obtained with a relatively high transparency to visible light but low mechanical strength due to large tensile residual film stress.

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الطرق التكنولوجية لتكوين الرقيقة فى وجود البلازما المنخفضه الحرارة

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ملخص البحث

يتم فى هذا البحث استعرض العلاقة بين كل من نمو وتكوين الأفلام الرقيقة ومتغييرات طرق التكوين المختلفة . وتستخدم مثل هذه العلاقة كدليل تحضيرى عند تجهيز بعض الأفلام الرقيقة ذات خواص معينه. ويعتبر اختبار تقنية تكوين مثل هذه الأفلام من العوامل المؤثرة ، التى يجب أن توضع الاعتبار. ويعطى هذا البحث خواص وتطبيقات استخدام تقنيات التكون فى وجود وسط من البلازما عند درجتى حرارة وضغط منخفضتين . كذلك يتم تقديم طريقة تكوين أفلام رقيقة مكونة من السيليكون والنيتروجين على قاعدة من السيليكون باستخدام الطريقة الكيميائية لترسيب الغازات ، وذلك باستخدام غاز السيلان المخفف فى غاز النيتروجين فقط فى وجود وسط من البلازما عند درجتى حرارة وضغط منخفضتين . وتعتبر هذه الطريقة معاكسة للطرق السابق استخدامها والتى تستوجب وجود درجة حرارة مرتفعة قد تصل الى ٧٠٠ درجة مئوية . ومن أهم خواص الأفلام الرقيقة التى تم الحصول عليها الدرجة العالية النسبية من الشفافية للضوء المرئى ولكن ذات مقاومة ميكانيكية منخفضة .