Flexible system for multiple plasma immersion ion implantation-deposition processes

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Multiple plasma immersion ion implantation-deposition offers better flexibility compared to other thin film deposition techniques with regard to process optimization. The plasmas may be based on either cathodic arc plasmas (metal ions) or gas plasmas (gas ions) or both of them. Processing parameters such as pulsing frequency, pulse duration, bias voltage amplitude, and so on, that critically affect the film structure, internal stress, surface morphology, and other surface properties can be adjusted relatively easily to optimize the process. The plasma density can be readily controlled via the input power to obtain the desirable gas-to-metal ion ratios in the films. The high-voltage pulses can be applied to the samples within (in-duration mode), before (before-duration mode), or after (after-duration mode) the firing of the cathodic arcs. Consequently, dynamic ion beam assisted deposition processes incorporating various mixes of gas and metal ions can be achieved to yield thin films with the desirable properties. The immersion configuration provides to a certain degree the ability to treat components that are large and possess irregular geometries without resorting to complex sample manipulation or beam scanning. In this article we describe the hardware functions of such a system, voltage–current behavior to satisfy the needs of different processes, as well as typical experimental results. © 2003 American Institute of Physics.

I. INTRODUCTION

Pulsed plasma-based ion implantation (PBII) encompassing plasma immersion ion implantation (PIII) and vacuum arc plasma deposition is quite versatile. Plasma immersion ion implantation-deposition (PIII-D) was first proposed by Brown et al. to fabricate a metal film using pure metal plasmas. In the process, the implantation and deposition phases are determined by the presence or absence of a high-voltage pulse applied to the substrate. Film adhesion is improved due to metal ion mixing of the deposited layer. According to Anders, this technique offers much flexibility, for example, by choosing the ratio of deposition and implantation phases, ion energy and projected range, ion beam mixing of deposited film and substrate, etc.

PIII-D can also be used to fabricate compound films by the addition of reactive gases. For example, synthesis of Al2O3, AlN, TiO2, and TiN (Ref. 7) has been reported. Most of these experiments are performed in a gaseous atmosphere and the compound films are usually formed by reactions preferentially occurring on the substrate surface or by implantation and deposition of the gas ion species induced by the vacuum arc at higher gas pressures. The processes are normally controlled by adjusting the gas pressure. However, the gas pressure also affects the vacuum arcs, plasma transfer, ion charge state, and surface reactivity, consequently making processing optimization quite complex. Tian et al. have employed nitrogen plasmas, not nitrogen gas, to fabricate TiN films in a process in which the plasma parameters can be separately controlled independent of the vacuum arcs. Recently, we have improved the pulsing power supply and other hardware to enhance the versatility of the pulsed-plasma PIII-D process. In this article the characteristics of the hardware and typical processes are presented.

II. HARDWARE AND PROCESSES

The basic plasma PIII-D equipment has been described elsewhere. In this investigation, the system has been upgraded to conduct PIII-D in a more flexible manner. As for the power modulator, the maximum pulse width has been extended to 2 ms from several hundreds of microseconds. In this instrument, not only can pure metal ion implantation without deposition be carried out, but also it is possible to implant many gas ions using multiple plasmas to tailor the film composition and structures. The function of electrical phase shift is enhanced so that the implantation pulse does...
not need to be applied within the cathodic arc duration as in the old mode. In the present setup, implantation can be performed either before or after the cathodic arc duration. In this way, gas ion mixing effect (without metal ion) can be exclusively achieved. A new set of filaments is used to ensure that a higher heating power can be applied to produce a higher plasma density. This may enlarge the changeable zone of the plasma density. In older systems, the filament holder is typically of Teflon which sometimes cracks when the heating power is high and this can limit the plasma density. In the newly designed filaments, the holder is made of soldered ceramics that can tolerate a much higher temperature and consequently, the filaments can be operated at higher current to achieve higher plasma density. All in all, compared to older and conventional PIII systems, the new improvements provide easier control of the implantation versus deposition phases and the operation range is wider such that more flexible PIII-D processes can be more readily conducted. In practical applications, the vacuum arc produces metal plasmas and the hot filament glow discharge or rf plasma source generates gas plasmas. The high voltage is applied to the sample to carry out ion implantation. As shown in Fig. 1, the relative pulse and processing parameters may arbitrarily be combined and the novel features are designated by an asterisk in the figure. Consequently different ion beam assisted deposition (IBAD) processes can be conducted using the improved hardware, and process optimization such as improvement of the film adhesion, internal stress control, and hybrid treatment capabilities can be readily implemented without breaking vacuum.

A. Multiple plasma PIII-D

The mechanism of implantation-deposition processes conducted in plasmas is considerably different from that in a nonplasma environment such as PVD or PIII-D employing only a cathodic arc. In a plasma environment, more excited neutrals in addition to charged particles can reach the sample surface due to the higher reactivity in plasma environment and also the applied electric field. Thus the average ion flux that can be adjusted by altering the plasma density, pulsing frequency, pulse duration, and applied voltage is higher, and ion mixing can be achieved by using one or several ion species including metal ions from the cathodic arc sources. For instance, ion mixing can be conducted using either gas ions alone or gas plus metal ions according to the experimental conditions. The flexibility to change the experimental parameters has an appreciable effect on the achievable surface morphology, structure, and internal stress in the samples. In contrast, in a nonplasma environment, the adsorption process is dominated by the arrival probability of gas molecules at the surface and is primarily related to the working pressure. Ion mixing is usually attained using the incident metal ions. This is not as favorable with respect to optimization of the surface properties and morphology compared to that in a plasma environment. For instance, higher energy nitrogen ion mixing may lead to a larger grain size, but on the other hand, our results using titanium/nitrogen ion mixing show smaller grain sizes at higher energy, perhaps a consequence of simultaneous adsorption and implantation. It should be noted that a vacuum arc also induces some ionization of the gas species, as inferred in Fig. 2. The implantation current does not drop abruptly to zero after the vacuum arc has been turned off and exact control and optimization of the process may not be as straightforward in this manner.

B. Plasma density

The composition of the plasma can be changed by the power of the plasma sources. In plasma IBAD, the composition of the deposited film can be optimized for superior surface properties while the ion species and flux used for ion mixing can be independently changed. Therefore a gradient film can be tailored by simply controlling the ratio of the ions using different plasma densities. This is similar to conventional IBAD in which the gradient layer is obtained by adjusting the ion/atom arrival ratio. Previous experiments have shown that a gradient film can effectively yield superior surface properties.

C. Pulse phases

In plasma IBAD, the phase of the sample bias pulse can be adjusted independent of that of the cathodic arc and many different ion mixing schemes can be implemented. As shown
in Fig. 3, pure nitrogen plasma implantation can be achieved when the implantation and vacuum arc pulses do not overlap. This leads to an alternating process of metallic ion deposition and nitrogen implantation (ion mixing). In comparison, dual ion mixing (metallic ion and gas ion) effects can be attained when the implantation pulse lies within the vacuum arc pulse, assuming that the implantation pulse duration is smaller than that of the cathodic arc. Figure 4 displays an example of such a process in which the ion mixing effect is stronger. Usually, the deposition rate is lower due to more severe sputtering and better power supplies are required to allow for more flexible synchronization of the implantation and cathodic arc phases. In conventional PIII-D with or without reactive gases, but not in a plasma environment, the implantation pulse typically varies within the vacuum arc pulse duration, and shifting the implantation pulse out of the cathodic arc pulse serves no particular purpose since there are no charged particles at that point. Therefore incorporation of gas plasma renders the process more flexible and versatile.

D. Pulse duration

In PIID, whether there is deposition is determined by the implantation pulse duration and relative phase (implantation versus arc pulse). With a longer implantation pulse (longer than the arc duration), pure implantation incorporating metal and gas ions can be accomplished, as indicated in Fig. 5. In this way, there is no metal film deposited onto the substrate due to the high bombardment energy and severe sputtering. As systematically investigated by Anders, most metal ions possess multiple charge states (higher than +1). This may be favorable for better ion implantation effects. For example, titanium ions have an average charge state of 2.2, consequently a 20 kV sample bias leads to a resultant bombarding energy of 44 keV. In contrast, by properly adjusting the duration and relative phase, a metallic layer can be formed with proper ion mixing using dual ions as shown in Fig. 4. A small ratio of the implantation duration to arc duration is recommended if a compound layer, e.g., TiN is desired. A ratio that is too high cannot result in such a layer, as simulated by Anders due to sputtering effects. However, in our case with nitrogen plasma, a high ratio may still be feasible since TiN possesses a lower sputtering rate than pure titanium.

E. Pulsing frequency

In most of our previous PIID experiments, the sample bias frequency and cathodic arc frequency are the same, but it does not have to be so. We have recently used different frequencies to optimize low-pressure nitriding. The electrical behavior is shown in Fig. 6. This process is similar to the one described by Anders in which many implantation pulses exist in each vacuum arc duration, but in our experiments,
the implantation pulses also exist between the lower frequency vacuum arc pulses (up to 50 Hz) to achieve nitrogen incorporation.

Titanium nitride films possess higher wear resistance and have found many applications in the industry. We have synthesized titanium nitride films using different processing techniques including plasma PIII-D and the surface features are parameter dependent. The ion mixing voltage using dual plasmas crucially affects the surface properties. As an example, the effects of the implantation voltage variations on the surface properties are shown in Fig. 7. The ion mixing voltage using dual plasmas crucially affects the surface properties although the layer thickness does not vary significantly. The surface roughness and grain size of the films decrease with a higher voltage. On the other hand, the corrosion and tribological properties bear a different relationship with the voltage, and a higher voltage actually leads to better wear resistance but worse corrosion resistance. It has also been observed that the deposition rate is much higher using nitrogen plasma compared to the nonplasma conditions. This can be attributed to the difference in the sputtering rate.

We have modified our plasma immersion implanter to perform flexible plasmasbased ion beam assisted deposition. By carefully selecting the experimental parameters such as plasma density, pulse width, synchronization of the cathodic arc and sample bias pulses, and others, pure deposition, pure implantation, and IBAD can be accomplished. The improved hardware design enables versatile and user-friendly operation. A myriad of thin films with attractive properties have been fabricated using this technique. The flexibility intrinsic to the technique makes it relatively easy to optimize individual processes and materials properties such as internal stress, structure, surface properties, etc.

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