

Nanocomposite Thin Films for both Mechanical and Functional Applications

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Abstract—The design methodology and realization of nanocomposite films aiming for mechanical (superhardness, toughness) and functional (optical, microelectronic) properties were discussed in this paper. Superhard TiCrCN and nc-TiN/a-SiN_x films and super-tough nc-TiC/a-C(Al) films were prepared through co-sputtering method by optimal design of microstructure. The nanocrystalline silicon (nc-Si) passivated with a matrix of thermally grown silicon dioxide were prepared using implantation of Si into SiO₂ film, and showed improved photoluminescence and optical properties. Also discussed is the nano-composite design of thin film resistor with optimized temperature coefficient of resistivity.

Index Terms— Nanocomposite; Films; Superhardness; Toughness; photoluminescence; Optical

I. INTRODUCTION

Nanocomposite films comprise at least two phases, a nanocrystalline phase and an amorphous phase, or a nanocrystalline phase with another nanocrystalline phase. The nanocomposite films have received much attention recently because they have unique physical-chemical properties [1~4], improved mechanical [5~7], electronic [8, 9], and magnetic [10] properties owing to the size effect [11~13]. That makes them attractive for industrial applications in high-speed machining [5,7], tooling [7,14], optical applications [8,9] and magnetic storage devices [11-13]. Design of the nanocomposite films needs the considerations of many factors, for examples, the interface volume, crystallite size, surface and interfacial energy, texture, epitaxial stress and strain, etc., all of which depend significantly on the material selection, deposition methods and process parameters. The most promising techniques for preparation of nanocomposite films are magnetron sputtering and chemical vapor deposition (CVD) [15], although other methods, such as laser ablation [16], thermal

evaporation, ion beam deposition [17] and ion implantation [18], are also used by various researchers. In this paper, the design concepts and characterization of several types of nanocomposite films were introduced, aiming for superior mechanical (superhardness, supertoughness, low residual stress, friction) and functional (optical, magnetic, microelectronic, biological, etc.) properties.

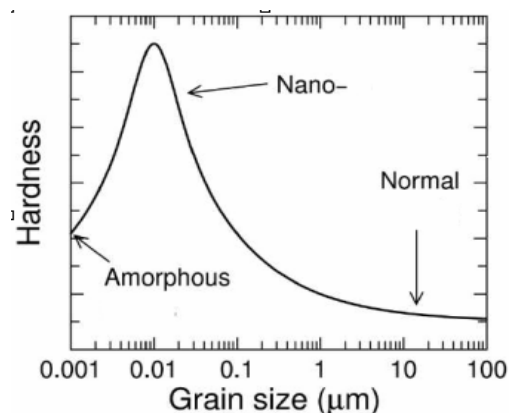


Fig. 1. Hardness evolution with change of grain size

II. NANOCOMPOSITE DESIGN FOR SUPERHARDNESS

Grain boundary hardening is one of the ways in hardening a film. The “Hall-Petch” relationship describes how grain size refinement increases the hardness of a material: $H(d) = H_0 + Kd^{-1/2}$, which also holds for thin films and coatings. The significant reduction in grain size to nano-meter scale could bring about the significant increase in hardness and strength as shown in Fig. 1. However, a new deformation mechanism, grain boundary sliding, dominates the deformation process when the grain size is down to a few nanometers, causing the significant decrease in film hardness (see Fig. 1). Further increase in film hardness or strength beyond this size limitation can only be achieved if grain boundary sliding is prevented through proper film design, i.e., by increasing the complexity and strength of grain boundaries in the nanocomposite films. This can be realized by optimal design of multiple phases, thus maximizing interfaces and formation of well-defined interfaces with high cohesive strength. It is better to use ternary, quaternary or even more systems, with a

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combination of high strength amorphous matrix and different types of refractory and immiscible metal-nitride nanocrystals to increase grain boundary complexity and strength.

One popular design method is to embed nanocrystalline phases in an amorphous matrix as shown in Fig. 2. Fig. 3 shows the potential hard materials for nanocomposite film design. Diamond like carbon (DLC), amorphous carbon nitride or other hard amorphous materials have been recognized as the primary candidates for the amorphous matrix, while nano-sized refractory nitrides, such as TiN, CrN, Si₃N₄, AlN, BN, etc. could be used as strengthening phases.

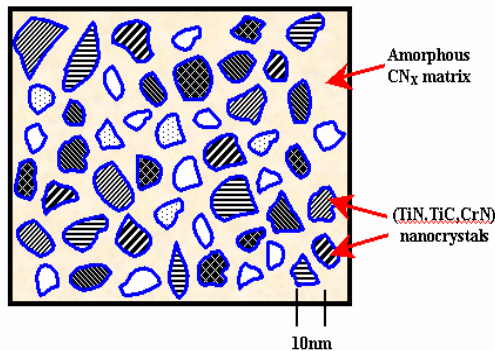


Fig. 2. The nanocomposite design with nanocrystals embedded inside an amorphous matrix

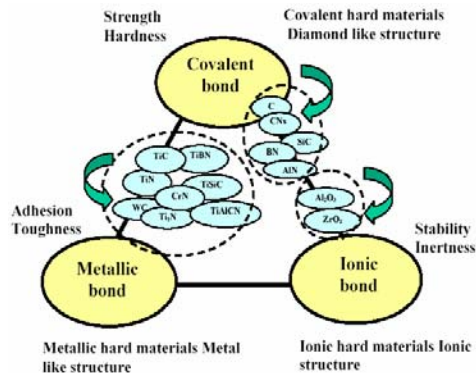


Fig. 3. Hard materials for nanocomposite coatings in the bond triangle and changes in properties with chemical bonding

One of the examples is the nanocomposite (Ti, Cr)(CN)/a-C film, which were prepared through co-sputtering of Ti, Cr and graphite targets in an argon/nitrogen atmosphere [19]. Fig. 4 shows one TEM image of the nanocrystals of TiN, CrN, TiC, (Ti,Cr)CN, et al with dimensions about 5-12 nm embedded in amorphous matrix of C and CN_x. These crystals have different orientations and lattice spacings. The average distance between these nanocrystals is about 8 to 10 nm. The film hardness can reach 40 GPa. Tribological tests using a ball-on-disk tribometer showed that the films demonstrated properties of low-friction and good wear resistance.

Another example is nc-TiN/a-Si₃N₄ nanocomposite films, prepared by co-sputtering Si₃N₄ and Ti targets in Ar/N₂ atmosphere [20]. Silicon nitride films (SiN_x) stays

amorphous even at high temperature of 1100°C and possess a desirable structural flexibility. Nanocrystalline TiN (or nc-TiN) crystallites can significantly enhance the hardening effects. TEM observation together with selected diffraction patterns reveal that with silicon content less than 23-32 at.%, TiN crystallites are observed embedded in an amorphous SiN_x matrix. Above 32.52 at.%Si, the amorphous phase dominates the film, thus no nanocrystallites are observed. Fig. 5 shows the relationship between film hardness together with crystallite fraction as a function of silicon content [20]. The film hardness increases significantly to approximately of 37 GPa at approximately 15 at% Si, corresponding to the maximum crystallite fraction. A further increase in silicon brings about drastic decrease in hardness to approximately 15 GPa which is the common value for the Si₃N₄ film.

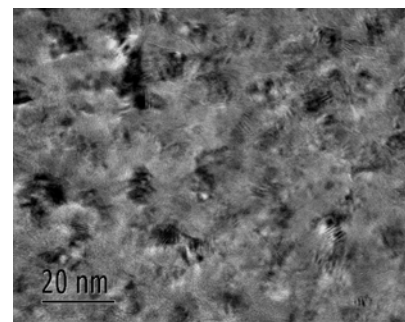


Fig.4. TEM image of the nanocrystals of TiN, CrN, TiC, (Ti,Cr)CN, et al with dimensions about 5-12 nm embedded inside amorphous matrix of C and CN_x [19]

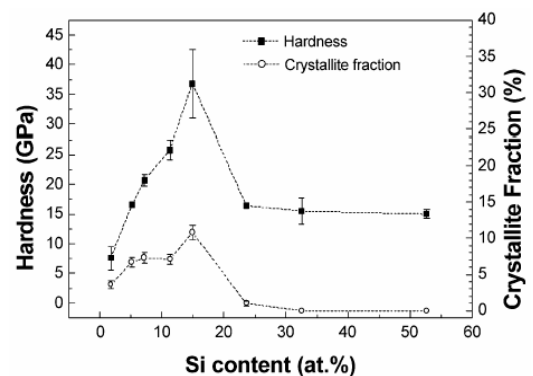


Fig. 5. Relationship between film hardness and crystallite size vs. Si contents for nc-TiC/ a-SiN_x film [20]

Fig. 6 demonstrates the relationship between nanoindentation hardness vs. crystallite size. As crystallite size decreases to a few nanometers (going from right to left on X-axis), the film hardness increases drastically (Hall-Petch relationship) because dislocation movement is hindered [21]. The film hardness peaks at about 7 nm crystallite size. Further decrease in crystallite size brings about decrease in hardness (the “anti-Hall-Petch” effect). The hardness tails off to that of an amorphous phase as crystallite size diminishes because of grain boundary sliding.

The above results clearly indicate that the grain size reduction is the dominant factor for the increase in film hardness.

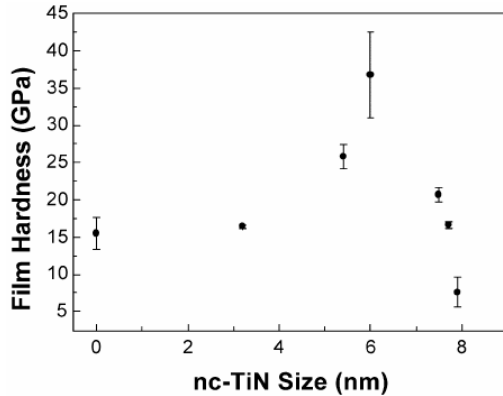


Fig. 6. Relationship between film hardness vs. TiN grain size for nc-TiC/Si₃N₄ film [20]

III. NANOCOMPOSITE DESIGN FOR SUPERTOUGHNESS

Apart from superhardness, good mechanical properties of the nanocomposite films also depend strongly on high fracture toughness. It is quite straightforward to think that high fracture toughness can be obtained in the nanocomposite films due to the nano-size grain structure and deflection, meandering and termination of nanocracks [22]. However, in order to obtain superhardness, usually plastic deformation is strongly prohibited, and dislocation movement and grain boundary sliding are dramatically prevented, thus probably causing loss in ductility.

There are two ways of increasing the film toughness. One is to maximize the film matrix toughness. Ceramic nanocrystals are often embedded into metal matrix, such as TiN in Ni [23], ZrN in Cu [24, 25], CrN in Cu [26], etc. to improve toughness and hardness. However, the metal matrix solution may still render poor thermal stability problems, and dislocation movement initiated from grain boundaries may be prohibited because of the small separation of grains in the metal matrix. Amorphous phase is often readily used as a matrix for high toughness and high hardness. Amorphous carbon (a-C) or diamond like carbon (DLC) film has attracted much research interests in wide range of engineering applications, but its inherit problems of high residual stress and poor toughness limited its applications. Incorporation of metals, for example, Al, into hydrogen free DLC matrix has been shown to be an effective way to reduce the residual stress as shown in Fig. 7 [27]. However, the film hardness decreases dramatically with the doping of Al into a-C matrix. To restore the hardness, TiC is embedded in the a-C(Al) matrix in the form of nano-sized crystals [27]. The resultant coating is a thick nanocomposite with nanocrystalline TiC imbedded in amorphous carbon matrix doped with aluminum, or, nc-TiC/a-C(Al). Under the experimental conditions studied, the 3 μ m thick

nc-TiC/a-C(Al) coating exhibited moderately high hardness (about 20 GPa) but coupled with very high toughness (55 % of plasticity during indentation deformation), and very low residual stress (0.5 GPa) [27].

Another way of improving film toughness is to optimize the nanostructure. The grain size, volume percentage and distribution of nanocrystals in the amorphous structures can be optimized to obtain a compromise between superhardness and toughness. The distance between two nanocrystals should be within a few nanometers. Too large a distance easily causes cracking propagation in matrix, while too narrow a spacing causes interaction of atomic planes in the adjacent nanocrystalline grains. Also, the nanocrystalline grains should have random orientation (i.e. high angle grain boundaries) to minimize grain incoherence strain and facilitate grain sliding to release strain and thus obtain improved toughness. The amorphous phase must possess high structural flexibility in order to accommodate the coherent strain without forming dangling bonds, voids, or other flaws.

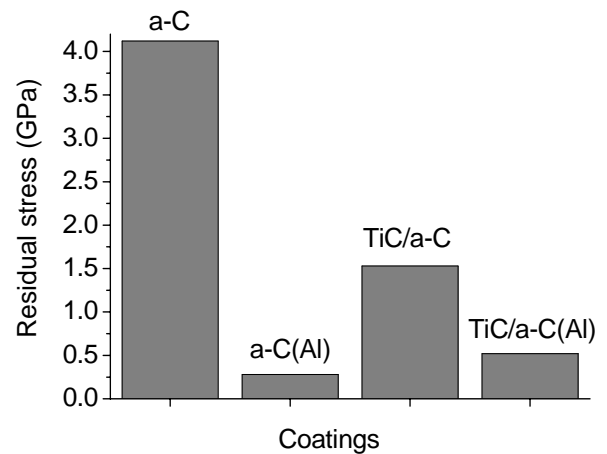


Fig. 7. Residual stress in the films of a-C, a-C(Al), nc-TiC/a-C and nc-TiC/a-C(Al) [27]

IV. NANOCRYSTALLINE DESIGN FOR FUNCTIONAL APPLICATIONS

Nanocomposite thin films also found themselves in functional applications. In these applications, usually metallic nanocrystallites, such as Cu, Ag, Au, Pt, Fe, Ni, Co, et al., are imbedded in an amorphous Al₂O₃, SiO₂, TiN, Si₃N₄ or TiO₂ matrix, with dramatically improved optical, microelectronic, and magnetic properties [28,29,30,31].

Recently SiO₂ films containing silicon nanocrystals have attracted much attention due to their potential applications in the areas of Si-based optoelectronic devices and single electron devices. Nanocrystalline silicon (nc-Si) passivated with a matrix of thermally grown silicon dioxide (SiO₂) can assure the localization of the photogenerated charge carriers. Ion implantation of silicon in amorphous SiO₂ films is a promising technique because of its ability of control of the

crystallites distribution and the full compatibility of the fabrication process with the mainstream CMOS process.

Fig. 8 shows the nano-crystals of Si imbedded in the amorphous SiO₂ matrix [32] achieved via Si via ion implantation. The substrate was a P-type (100)-oriented Si wafer, on which oxidation was carried out in dry oxygen at 950°C to grow an amorphous SiO₂ thin film with thickness of 30 nm. Then Si⁺ ions were implanted at 1 keV with the dose of 8×10¹⁶cm⁻² into the thermally-grown SiO₂ film. Thermal annealing was carried out in N₂ ambient for 30 minutes to induce crystalline formation.

The optical constants and the dielectric function of the Si nanocrystals are reduced significantly compared to those of the bulk crystalline Si [33] owing to the energy gap expansion of the nanocrystals as a result of the size effect. Fig. 9 compares the photoluminescence intensity of SiO₂ matrix with and without implanted with Si as well as after thermal annealing. Clearly the photoluminescence intensity increases dramatically with introduction of nanocrystals of Si [33].

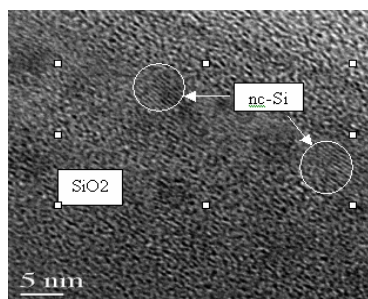


Fig. 8. High resolution TEM image showing the nanocrystals of Si embedded inside SiO₂ matrix [33]

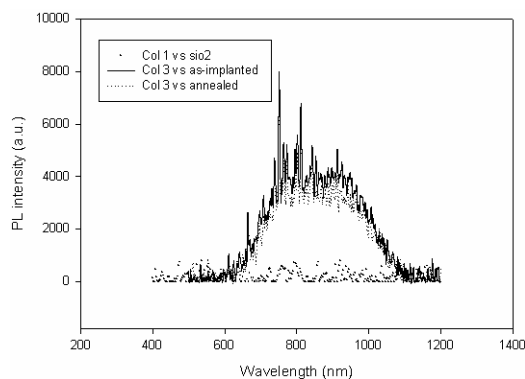


Fig. 9. The comparison of photoluminescence intensities of SiO₂ matrix with and without implanted with nano-Si crystals as well as after post annealing [33]

X-ray photoelectron spectroscopy (XPS) was used to characterize the existence and chemical states of the so-formed nanocomposite films, and the results are shown in Fig. 10 [34,35]. Fig. 10 (a) and (b) show the Si 2p XPS peaks on the film surface and after ion beam etching for different periods. From the decomposition of the Si 2p peaks, the relative concentrations of various components corresponding to different Si oxidation states Siⁿ⁺ (n = 0, 1, 2, 3, and 4) in the SiO₂ films were determined, and the

results are shown in Fig. 11. Results confirmed that except the Si nanocrystals (the corresponding Si oxidation state is Si⁰) and the stoichiometric SiO₂ (the corresponding Si oxidation state is Si⁴⁺) there are still other sub-oxides corresponding to the three Si oxidation states Siⁿ⁺ (n = 1, 2 and 3) in the Si-implanted SiO₂ films after high temperature annealing, which has not been reported previously.

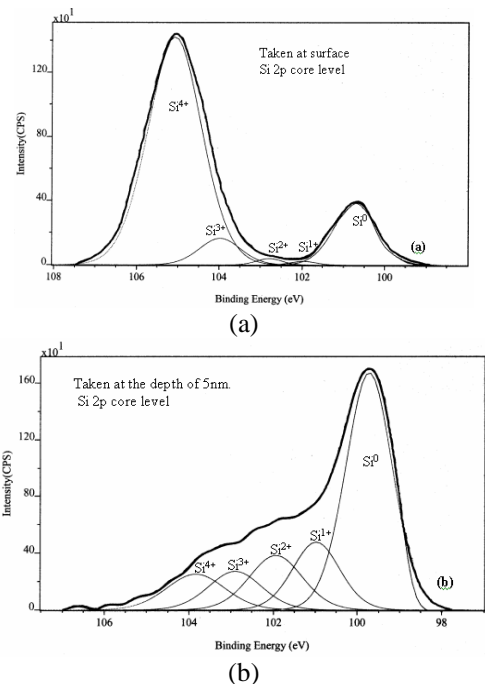


Fig. 10. Si 2p XPS peak deconvolution on the film surface and after ion beam etching to 5 nm for Si/SiO₂ nanocomposite film [35,36]

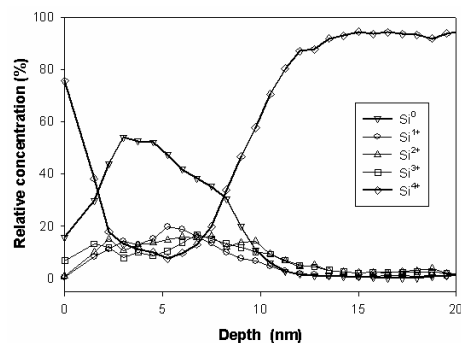


Fig. 11. XPS depth analysis of nanocrystalline Si/SiO₂ film showing the concentration evolution of different components [35,36]

Sputtered tantalum nitride films used as thin film resistors (TFR) have a wide variety of applications because the films have a wide range of electrical resistivity (ρ) and temperature coefficient of resistivity (TCR). The tantalum nitride normally has negative TCR values while copper would normally give positive TCR. It is reasonable to propose the nanocomposite TaN-Cu structure to demonstrate a near-zero TCR. In the nanocomposite film, Cu metal clusters embedded in a ceramic matrix with characteristic sizes on the order of a few nanometers show special properties for numerous potential applications [37]. When the cluster size is smaller than the electron mean free

path, electron scattering is almost completely caused by grain boundaries and hence both the electrical resistivity and TCR are expected to change dramatically. The TaN-Cu nanocomposite thin films can be prepared by reactive co-sputtering of Ta and Cu targets in a gas mixture of N₂/Ar [36]. The electrical properties of nanocomposite thin films are functions of N₂ flow rate, target power, Cu concentration and annealing time, and a near-zero TCR can be realized with a precise control of deposition parameters.

V. SUMMARY

Nanocomposite thin films are at the beginning of their development for a wide range of precision engineering applications in both mechanical and functional fields. In mechanical application aspect, superhard and super tough nanocomposite thin films are obtainable through optimal design of microstructure. In functional application aspect, nanocomposite thin films of nc-Si in amorphous SiO₂ obtained via ion implantation of Si into thermally-grown SiO₂ thin films demonstrate improved photoluminescence and optical properties. Nanocomposite thin films of TaN/Cu obtained by magnetron sputtering show near zero temperature coefficient of resistivity which has much significance in electronics applications.

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