Experimental and *ab initio* study of the mechanical properties of hydroxyapatite

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The authors have studied the elastic properties of radio frequency sputtered phase pure, stoichiometric, and dense hydroxyapatite films by nanoindentation. The measured elastic modulus values have been compared to *ab initio* calculated data. The calculation technique was based on the determination of all elastic constants. The calculated and measured elastic modulus values differ by ~10%. The good agreement indicates that the elasticity of hydroxyapatite can be described using *ab initio* calculations, establishing the elastic modulus thereof. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2738386]

Calcium phosphates are suitable materials for biomedical applications.[1] Especially hydroxyapatite, $Ca_5(PO_4)_3OH$ (space group $P6_3/m$, hereafter HA), is exploited for implants since it mimics mineral components of natural bone.[1] Major drawbacks of HA are associated with the inadequate mechanical properties of the bulk material: HA possesses a low fatigue resistance and is brittle, inhibiting its usage as implant in load bearing applications.[2] Therefore, HA coatings are usually deposited on a load bearing implant, mainly Ti and its alloys, in order to fulfill the mechanical requirements for load bearing applications, such as total joint replacements and dental root implants, by combining the mechanical strength of the bulk material and the biocompatibility of the HA coating.[3]

Despite its importance for biomedical applications, conflicting reports of the elastic properties of HA are found in the literature. The reported elastic modulus (E) values range from 3 to 180 GPa, over two orders of magnitude.[4–16] The main factors suggested to contribute to the spread of the reported elastic modulus values are the density,[4,5] the shape of the pores,[6] the crystallinity,[4] the grain size, and the purity[6] of the HA phase. Actually, the elastic modulus of HA samples is not reported together with a complete description of the sample in terms of density, chemical composition (Ca to P ratio, Ca/P) and structure which leads to difficulty in data evaluation. For example, powdered[7] and sintered bulk HA samples[8] for which E are 114 and 63 to 105 GPa, respectively, have only been characterized in terms of density (3.17 and 2.81 to 3.02 g/cm^{-3}, respectively) and phase composition (hexagonal HA, h-HA, in both cases), but not in terms of their composition. On the other hand, reports on HA thin films synthesized by laster ablation ($E=111$ GPa, Ca/P $=1.73$, h-HA)[14] and radio-frequency (rf) sputtering ($E=120$ GPa, Ca/P$=1.41$, h-HA and tricalcium phosphate)[16] contain no information about the material density. From these examples, it is evident that the elastic modulus value of phase pure, stoichiometric, and dense HA is unknown.

Possibly due to the comparably large unit cells containing 42 (fluoro- or chloro-apatite) or 44 atoms (HA), apatites have only recently been studied by quantum mechanical methods.[17] Since, in addition to their biological potential, these apatites possess capabilities for ion exchange for toxic waste storage,[17] calculations of the structural and electronic properties of HA have been carried out with respect to substitution of Ca by Zn and Cd (Ref. 17) as well as of OH and PO_4 groups by CO_3 groups.[18] However, to the best of our knowledge, no reports on the calculation of the mechanical properties of HA are available.

As the reported variation of the elastic modulus values ranges over two orders of magnitude and no report of the elastic properties of phase pure, stoichiometric, and dense HA has been communicated, we have grown this material by rf magnetron sputtering and measured its composition, structure, density, and elastic modulus. The measured properties are compared to *ab initio* calculated data to establish the elastic modulus of phase pure, stoichiometric, and dense HA.

HA coatings were deposited on electrically grounded silicon wafers by rf sputtering in a turbomolecularly pumped chamber with a base pressure of around 1.33×10^{-4} Pa (1×10^{-6} Torr). The deposition was performed in a pure Ar atmosphere at a pressure of 0.665 Pa (5 mTorr). The applied rf power density was 1.5 W/cm^2 to the sintered HA target. The target to substrate distance was 8 cm. The resulting coating thickness was determined by profilometry. The deposition rate was about 0.5 nm/min. With the aim to crystallize the HA coating, it was annealed for 1 h at 550 °C in air, according to the procedure proposed by Nelea *et al.*[15]

Grazing angle x-ray diffraction (GAXRD) using a Siemens D500 diffractometer, operated with 1° incidence angle, was used to analyze the constitution of the HA coating. The scan rate of 0.5 deg min^{-1} was chosen to maximize the peak-to-noise ratio and the 2θ scan was acquired from 20° to 50°. The film density has been evaluated, combining both time-of-flight energy elastic recoil detection analysis[19] (TOF-ERDA) and film thickness measurements. X-ray photoelectron spectroscopy (XPS) was used to measure the

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chemical composition of the HA coating. High resolution spectra in the Ca2*p* and P2*p* regions were recorded to calculate the Ca/P ratio. This ratio was derived from peak areas using photoionization cross section calculated by Wagner *et al.*[20] The elastic modulus was determined by nanoindentation in a nanotriboindenter instrument (Hysitron Inc.) equipped with a Berkovich tip. Data were processed using the Hysitron software providing load-displacement curves corrected for thermal drift and machine constants (frame compliance, transducer spring force, and electrostatic force constants). Load-displacement curves were analyzed according to the Oliver-Pharr method[21] by fitting a power law relationship to the unloading curve and determining the initial unloading stiffness. Applied loads ranged from 50 to 1000 μN (penetration depths=5 to 50 nm) which corresponds to a maximum penetration depth of ~10% of the coating thickness. In this region no significant dependence of the results on the penetration depth has been observed. A total of about 100 indentations were realized on three different samples in order to increase the statistics. The elastic modulus was calculated based on a Poisson ratio of 0.28 measured by ultrasonic method by Grenoble *et al.*[7]

Density functional theory was used within the Vienna *ab initio* simulation package (VASP), where ultrasoft pseudopotentials are employed.[22,23] The generalized gradient approximation was applied in all calculations. The integration in the Brillouin zone is done on special *k* points determined according to Monkhorst-Pack. Unit cell containing 44 atoms[18] were studied on a mesh of $7\times7\times7$ irreducible *k* points. The convergence criterion for the total energy was 0.01 meV within a 495 eV cutoff. Atomic positions (internal free parameters) and lattice parameters were relaxed. Full structural relaxation was carried out at every volume (V).[24] The energy-volume curves obtained were used to calculate bulk modulus (B) by fitting them to the Birch-Murnaghan equation of states.[25] The calculation technique used to determine the elastic properties of HA consists of calculating the independent elastic coefficients (C_{11}, C_{12}, C_{13}, C_{33}, and C_{55}) obtained according to the method developed by Fast *et al.*[26] Furthermore, the total and partial densities of states (DOSs) were calculated.

We deposited a 450±29 nm thick HA film by rf magnetron sputtering. It is known that dense HA films can be grown using this technique. However, the phase purity and composition of the film often remain a problem.[15,16] Furthermore, Ozeki *et al.*[27] reported Ca/P ratios of up to 2.4 for rf magnetron sputtered thin films which is a significant deviation from the stoichiometric value of 1.67.[15] This phenomenon results from the formation of calcium based phases such as tricalcium phosphate (TCP), tetracalcium phosphate (TTCP), or calcium oxide (CaO). Therefore, a synthesis strategy based on a systematic study of the correlation between deposition parameters (power and pressure) and film composition was implemented to ensure the deposition of stoichiometric films. Figure 1 shows the GAXRD patterns of the HA target, the as-deposited film, and the annealed film. For all diffractograms presented, all the diffraction lines are consistent with, *h*-HA.[28] Calcium apatites are known to crystallize in hexagonal (space group $P6_3/m$) and monoclinic (space group $P2_1/b$) forms depending on the stoichiometry, temperature, and synthesis pressure.[29] Only defect-free and stoichiometric HA possesses a monoclinic structure.[29] During energetic vapor condensation, often, nonstoichiometric and/or defective HA films are synthesized,[15,16] exhibiting a hexagonal structure.[30] The as-deposited film appears crystalline, since the (0002) and the $(21\bar{3}1)$ reflections can be detected. The (0002) peak was fitted using a pseudo-Voigt function and presents a full width at half maximum (FWHM) of 0.61°. After annealing, many other diffraction peaks corresponding to *h*-HA appear at 28.10°, 32.08°, 33.98°, 43.82°, 45.28°, 46.70°, and 49.43° indicating increased crystallinity which is consistent with an increase of the (0002) peak intensity by a factor of 5 and a reduction of its FWHM by a factor of 3. The corresponding Miller's indices are indicated in Fig. 1. Before and after annealing, a (0001) preferential crystallographic orientation where *c* axis is perpendicular to the surface is observed.[27] No other phase than *h*-HA has been observed in the diffractogram indicating a phase pure coating. This is in contrast to literature reports where, often, other phases than HA (i.e., CaO,[15] TTCP,[27] etc.) are detected in rf sputtered HA coatings. XPS measurements support this conclusion since it is revealed that the Ca/P ratio of 1.69±0.02 which is close to the stoichiometric ratio of 1.67 is obtained. The binding energy values for the P2*p* ($2p_{1/2}$ and $2p_{3/2}$ are overlapped) and the Ca2$p_{3/2}$ lines are measured to be 133.4 and 347.5 eV, respectively. These data are characteristic for HA.[31] The O1*s* line consists of two components at 531.0 and 532.3 eV which are assigned to OH and PO_4 groups and to adsorbed water, respectively.[32] Based on TOF-ERDA measurements, the HA film density has been estimated to be 3.28±0.22 g/cm^3. Therefore, the analyzed films are fully dense since the theoretical density of HA is 3.16 g/cm^3.[5] Nanoindentation of the deposited film has been carried out after annealing; the coating exhibits hardness and elastic modulus values of 10±1 GPa and 147±10 GPa, respectively.

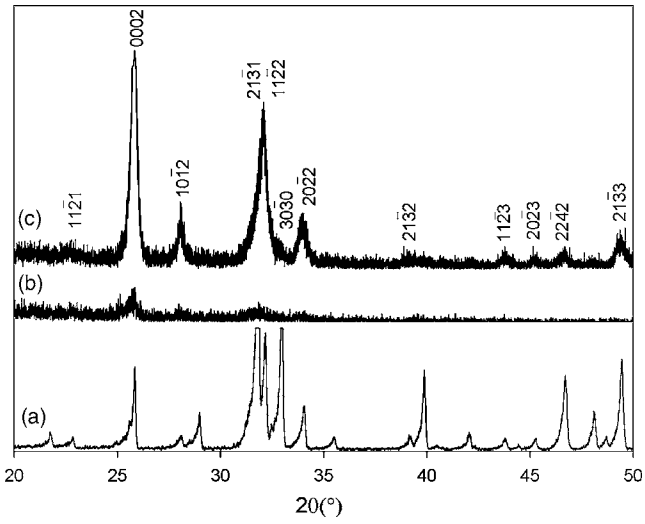

FIG. 1. (a) XRD patterns of HA target, (b) as-sputtered, and (c) annealed films.

To validate our experimental results, we calculated the elastic properties of HA. The calculated values for the lattice parameters (a and c) and equilibrium volume (V) are a=9.635 Å and c=6.595 Å and V=530.2 Å^3 which deviate by 2.2%, 4.2%, and 0.2%, respectively, from previously reported experimental values.[32] The bulk modulus B is in the range of 82 GPa, which accounts for a deviation of 6.4% from the experimental value determined for powdered HA,[10] where the density was not reported. The elastic constants were calculated to be C_{11}=117.1 GPa, C_{12}=26.2 GPa, C_{13}

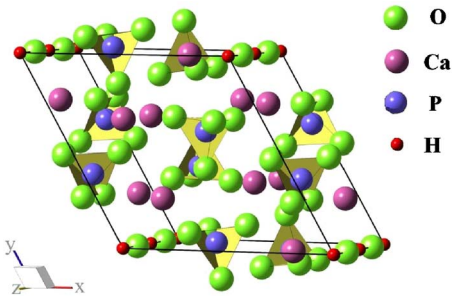

FIG. 2. (Color online) Hydroxyapatite structure viewed along the *c* axis, drawn using the coordinates of the relaxed cell from *ab initio* calculations. The size of the atoms has been chosen to facilitate the observation. The unit cell outline is defined by the black lines. The polyhedrons correspond to the PO_4 groups with a P atom in the center bonded to four O atoms. In order to facilitate the observation of the tetrahedrons, the cell was extended by 40% along the *a* and *b* axis.

=55.6 GPa, C_{33}=231.8 GPa, and C_{55}=56.4 GPa. The elastic modulus calculated based on the elastic constants is 132.1 GPa and Poisson's ratio was determined to be 0.23. Therefore, good agreement is obtained with the elastic modulus measurement values of dense, phase pure, and stoichiometric HA films presented here. The deviation between the calculated value of the elastic modulus and the one determined experimentally in the present work (dense, phase pure, and stoichiometric HA) is about 10%. The smallest deviation between the calculated elastic modulus value and the previously reported data for HA samples is 11% (Ref. 15) and 18%.[4,5] However, none of these reports contains chemical composition, phase purity, and density data. Our data indicate that the samples discussed in Refs. 4, 5, and 15 are, in fact, close to dense, phase pure, and stoichiometry HA.

The previously discussed mechanical properties of HA, namely, the fatigue resistance and the brittleness, can be understood by studying chemical bonding. Our analyses of partial DOSs (not shown here) reveal a strong ionic character of the interactions between the PO_4 tetrahedrons, the OH groups, as well as the Ca atoms, while covalent bonding is observed between P and O and O and H within the PO_4 and OH groups, respectively. This is consistent with results reported in the literature.[33] Therefore, the HA structure can be seen as a skeleton of PO_4 tetrahedrons connected with Ca and OH groups as already suggested for fluoroapatite[33] (Fig. 2). These results are supported by the chemical state data obtained by XPS. We suggest that the predominantly ionic interaction between Ca and PO_4 tetrahedrons, as well as OH groups, may be responsible for both the commonly observed brittle behavior and for the relatively poor fatigue resistance of HA.

In summary, using nanoindentation, we have determined the elastic properties of dense, stoichiometric, and phase pure HA films deposited by rf magnetron sputtering. *Ab initio* calculations have been used to calculate the elastic properties of HA. The calculation technique was based on the determination of all elastic constants. Detailed analyses of the deposited film show that we have synthesized stoichiometric, phase pure, and dense HA films. We have measured the elastic modulus of the deposited coating to be 147±10 GPa while calculated value of the elastic modulus was 132.1 GPa. Therefore, the deviation with our experimental data accounts for ~10%. Good agreement is thus obtained between experimental and calculated data indicating that the elasticity of HA can be described using *ab initio* calculations, establishing the elastic modulus of HA.

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